

# Electron and energy transfer in organic and hybrid systems

Dr. Arianna Marchioro and Prof. Frank Nüesch  
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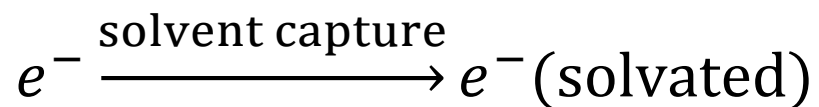
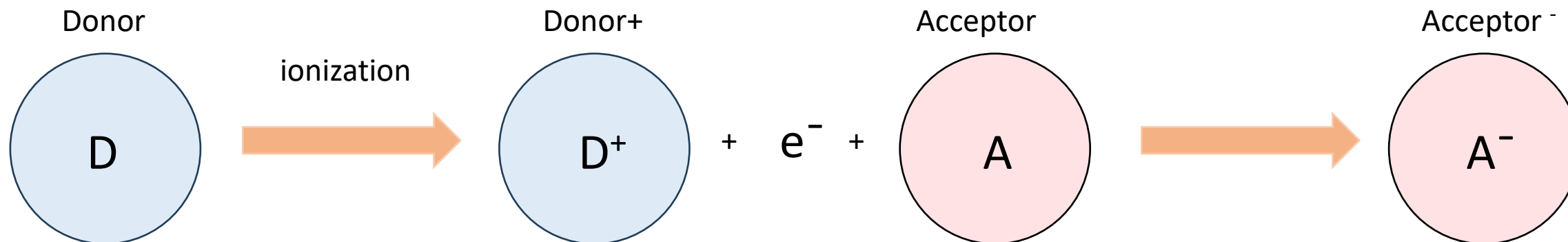
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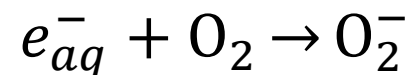
## Trivial electron transfer process



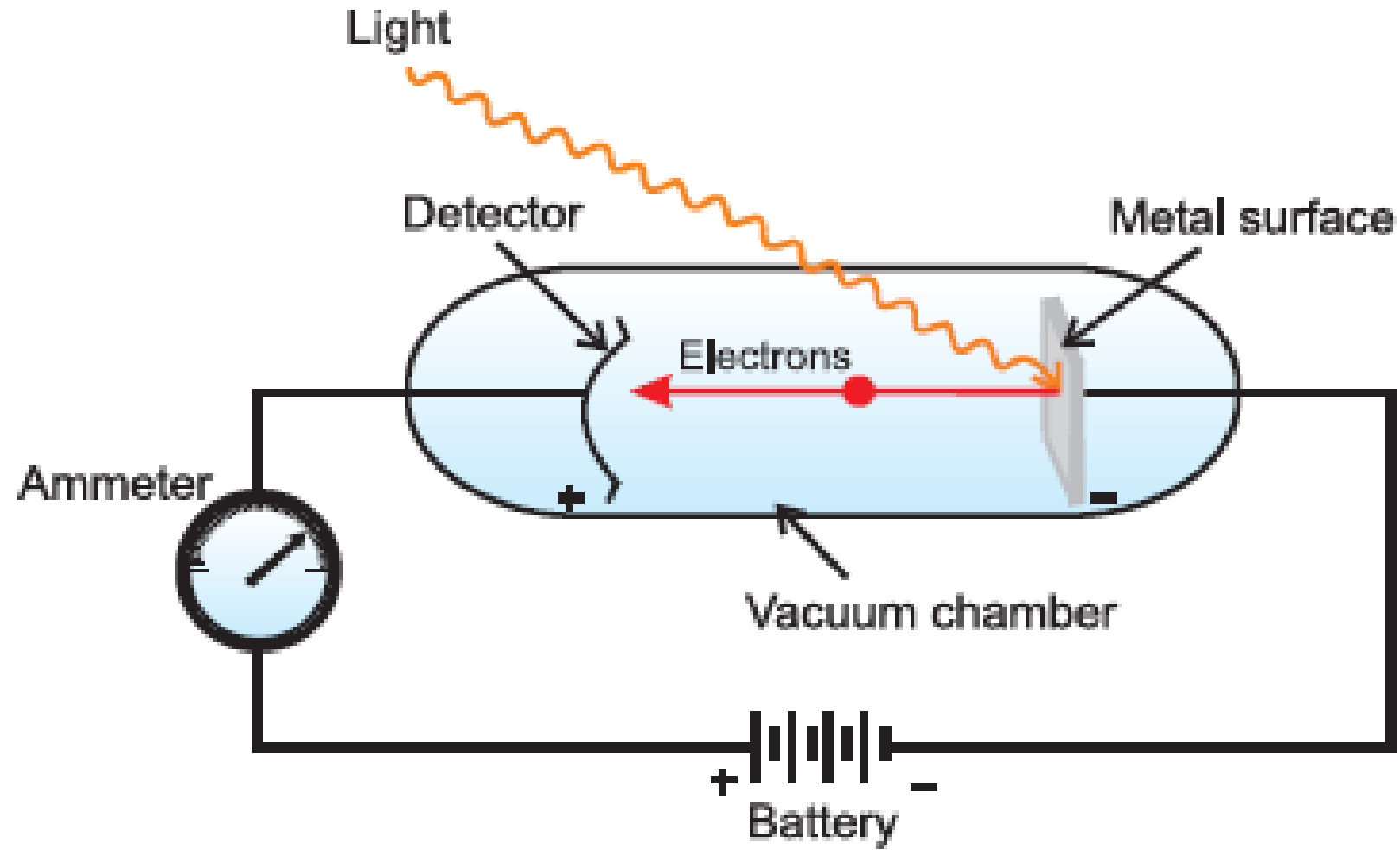
The hydrogen atom (radical) formed can undergo different reactions:



*Reduction of molecular oxygen (superoxide anion)*

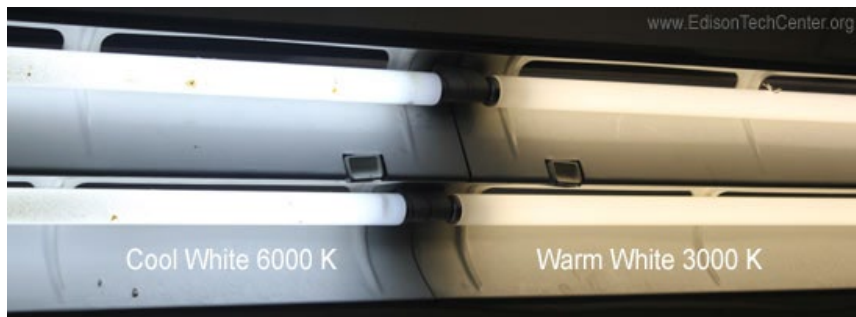
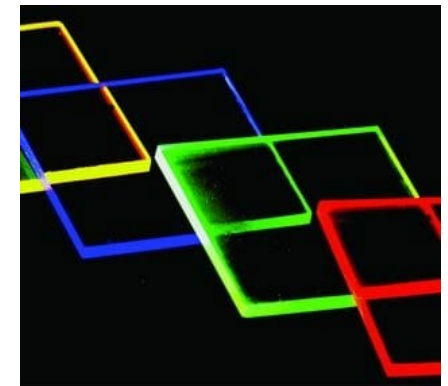
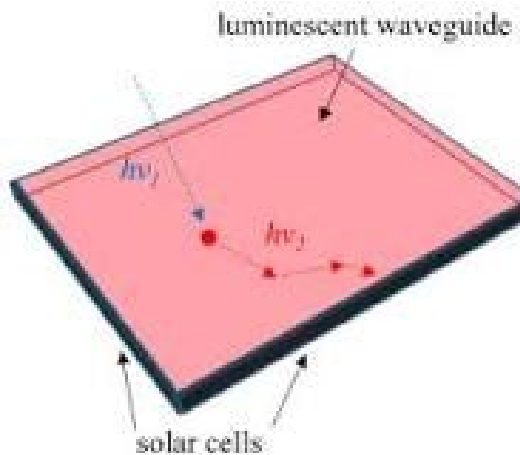
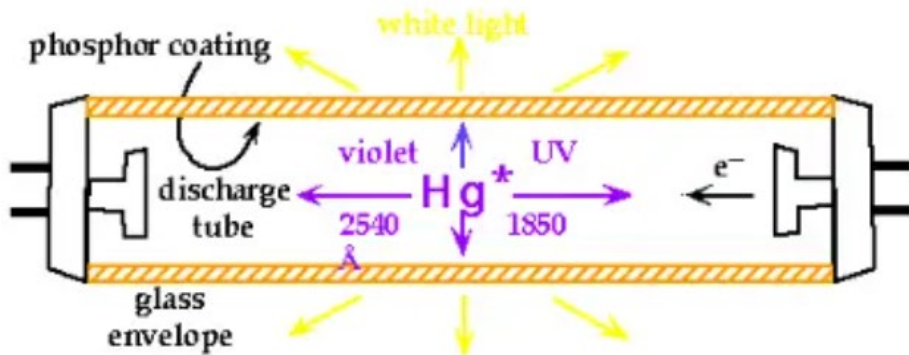
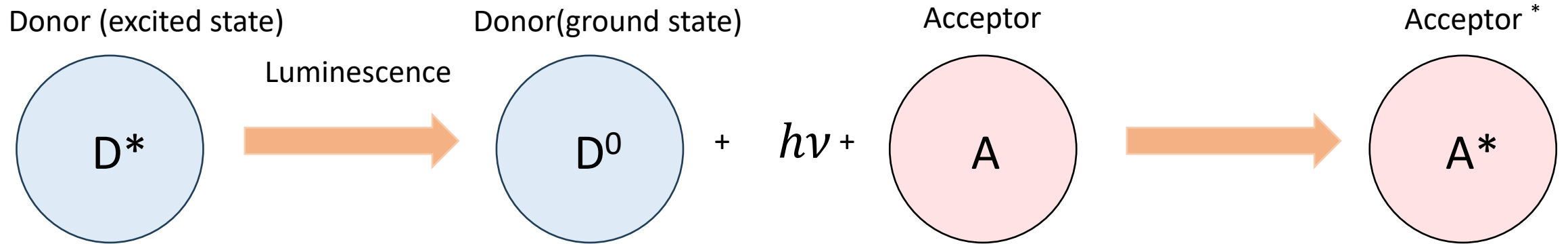


# Photoelectric effect

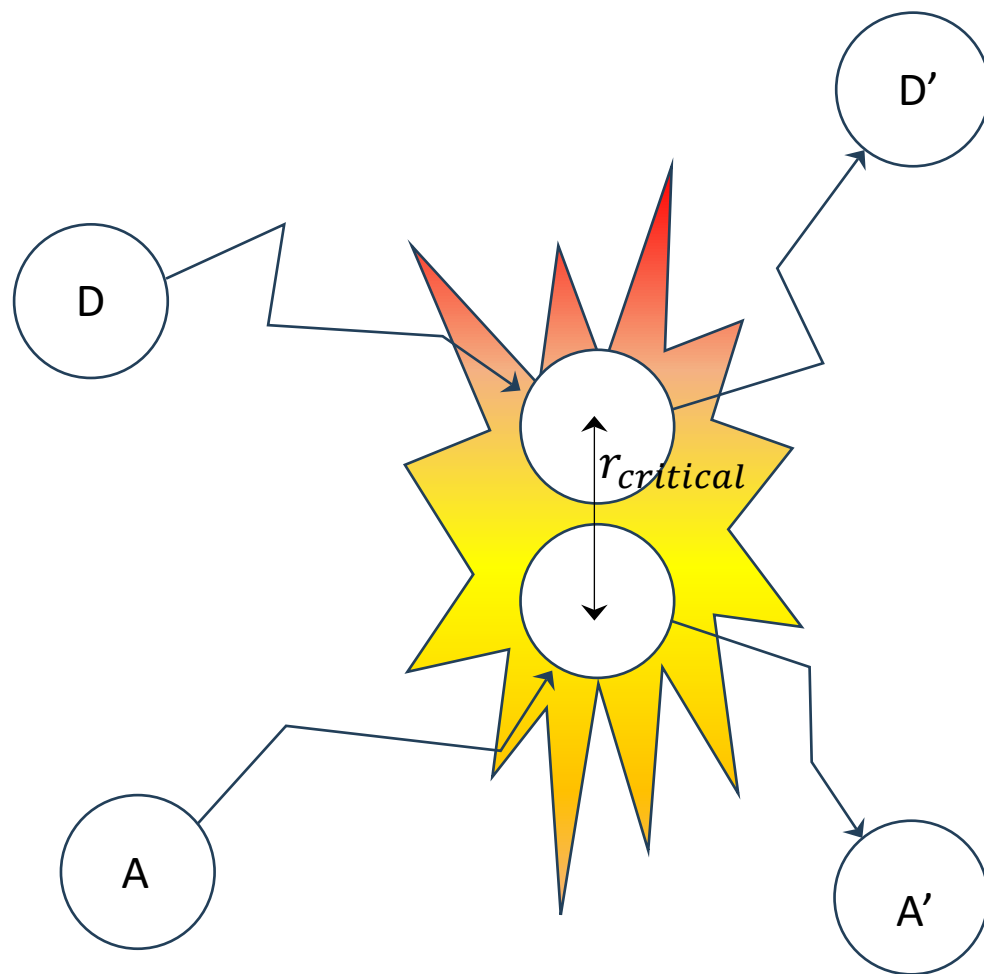


Nobel Prize (Einstein 1905)

# Trivial energy transfer process (radiative transfer)



# Formation of an activated complex



Diffusion rate constants can be estimated from the Smoluchowski-Stokes-Einstein equation:

$$k_{diff} = \frac{4RT}{3\eta} \left[ \frac{m^3}{mol \cdot s} \right]$$

For typical non-viscous organic solvents (benzene, acetonitrile, hexane) at room temperature,  $\eta \sim 1-10$  cP (1 Pa s = 10 P)

$$k_{diff} \approx 3 \cdot 10^9 - 3 \cdot 10^{10} M^{-1} s^{-1}$$

For electron and energy transfer requiring an activated complex, this is the fastest rate at which these processes can occur.

# Relation between thermodynamics and kinetics



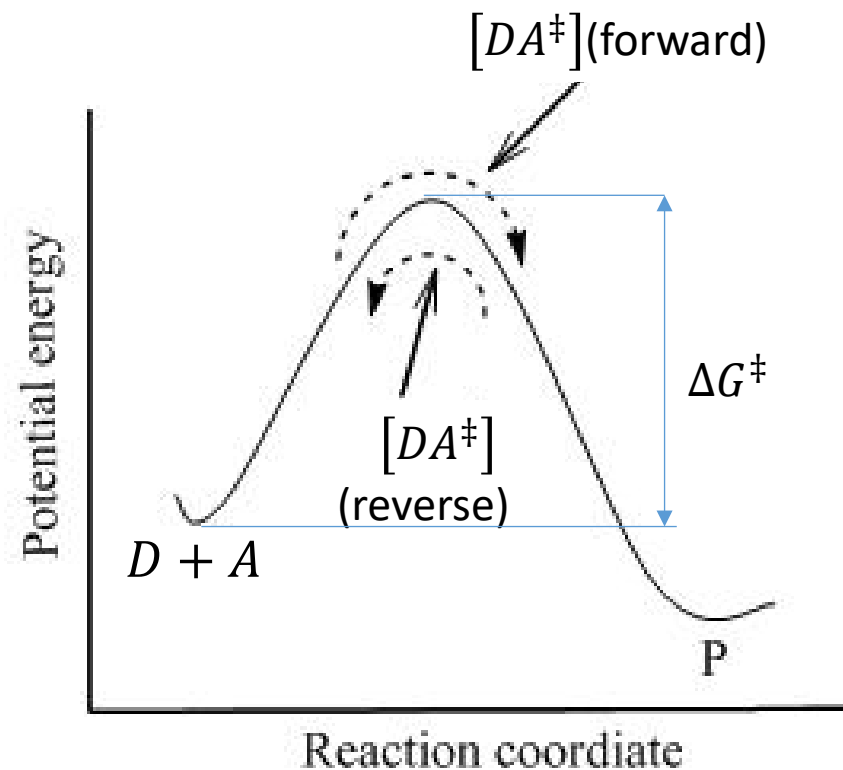
$$K^\ddagger = \frac{[DA^\ddagger]}{[D][A]} \quad \frac{d[P]}{dt} = k^\ddagger [DA^\ddagger] = k^\ddagger K^\ddagger [D][A] = k[D][A]$$

$$k = k^\ddagger K^\ddagger = k^\ddagger e^{-\frac{\Delta G^\ddagger}{RT}} = \kappa v e^{-\frac{\Delta G^\ddagger}{RT}}$$

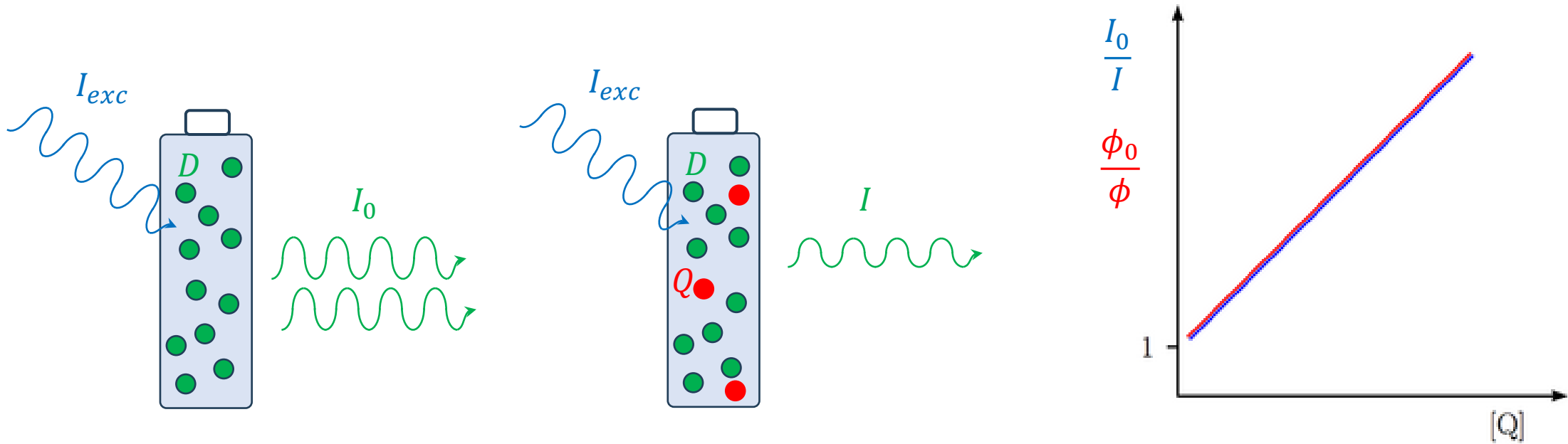
Using statistical mechanics

$$k = \kappa \frac{kT}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad \text{Eyring equation}$$

Transition state theory



# Kinetics of quenching



$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

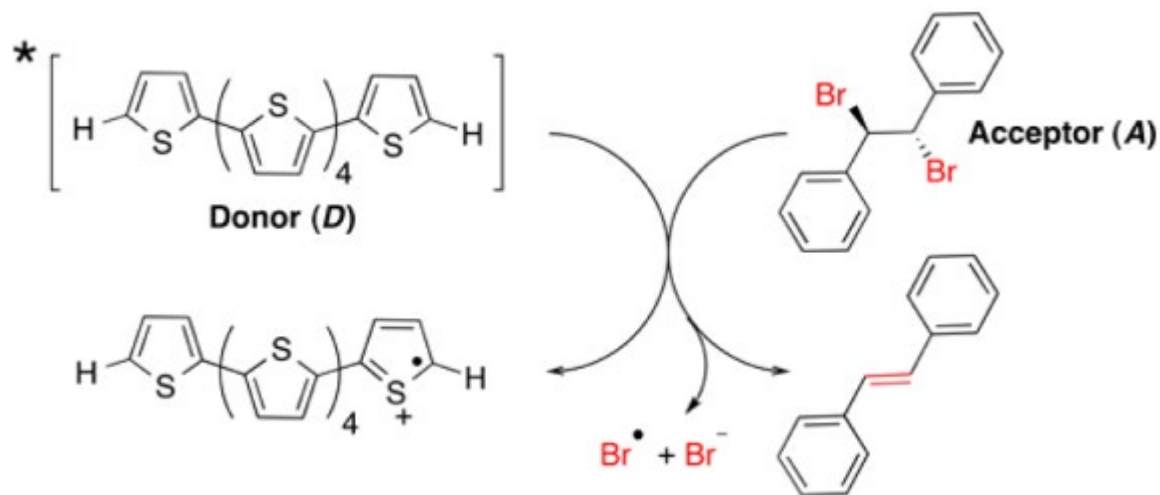
$$K_{SV} = k_Q \cdot \tau_{0,D}$$

Stern-Volmer equation

$\tau_{0,D}$  is the fluorescence lifetime of D in the absence of the quencher.  $k_Q$  is the bimolecular quenching constant (electron or energy transfer)

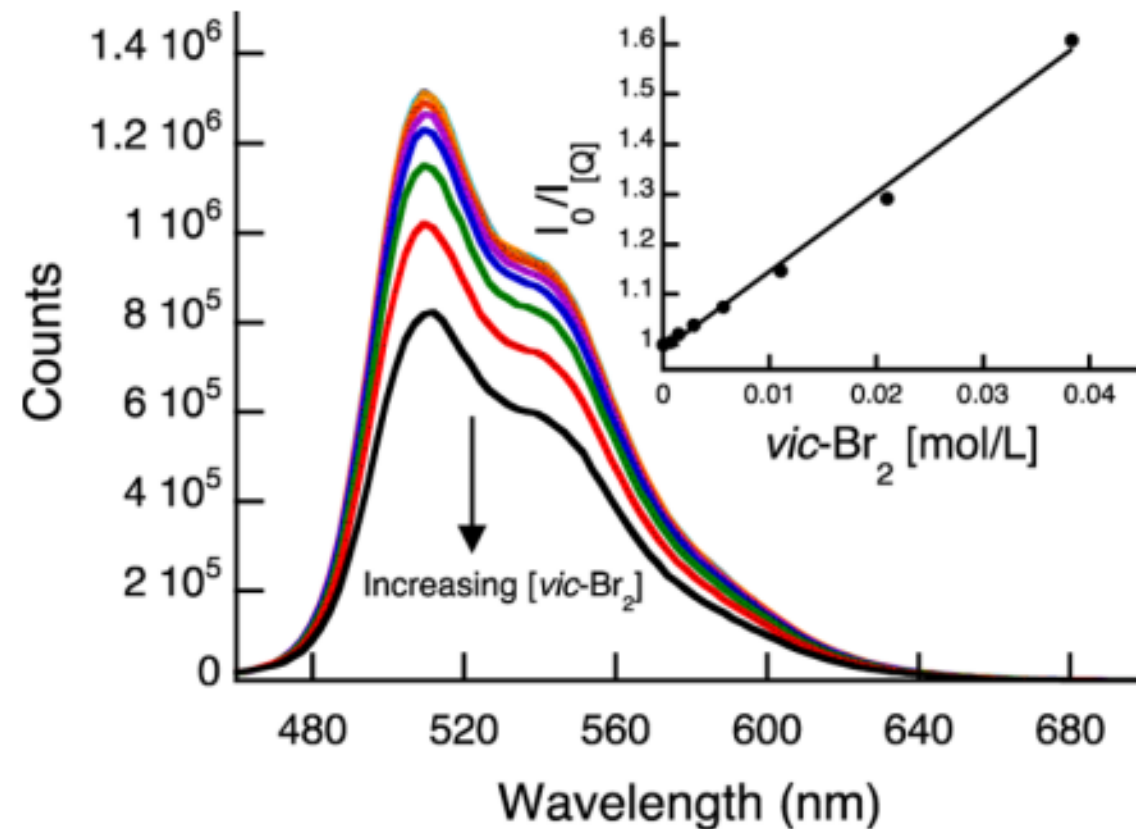
$I_0$  and  $I$  are the fluorescence intensities of the Donor with and without quencher, respectively.

# Photoinduced electron transfer

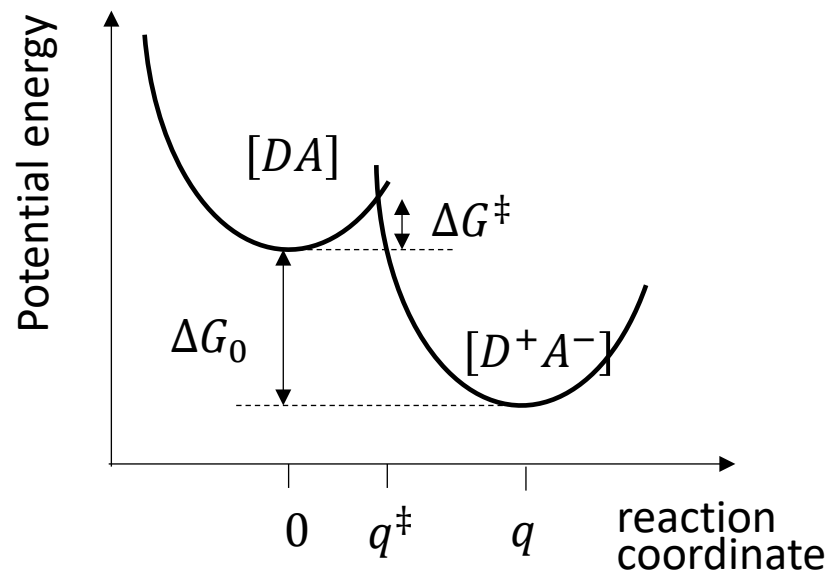


$$K_{SV} = 15.6 \cdot M^{-1}$$

$$k_Q = 1.93 \cdot M^{-1}s^{-1}$$



## Rehm-Weller plots

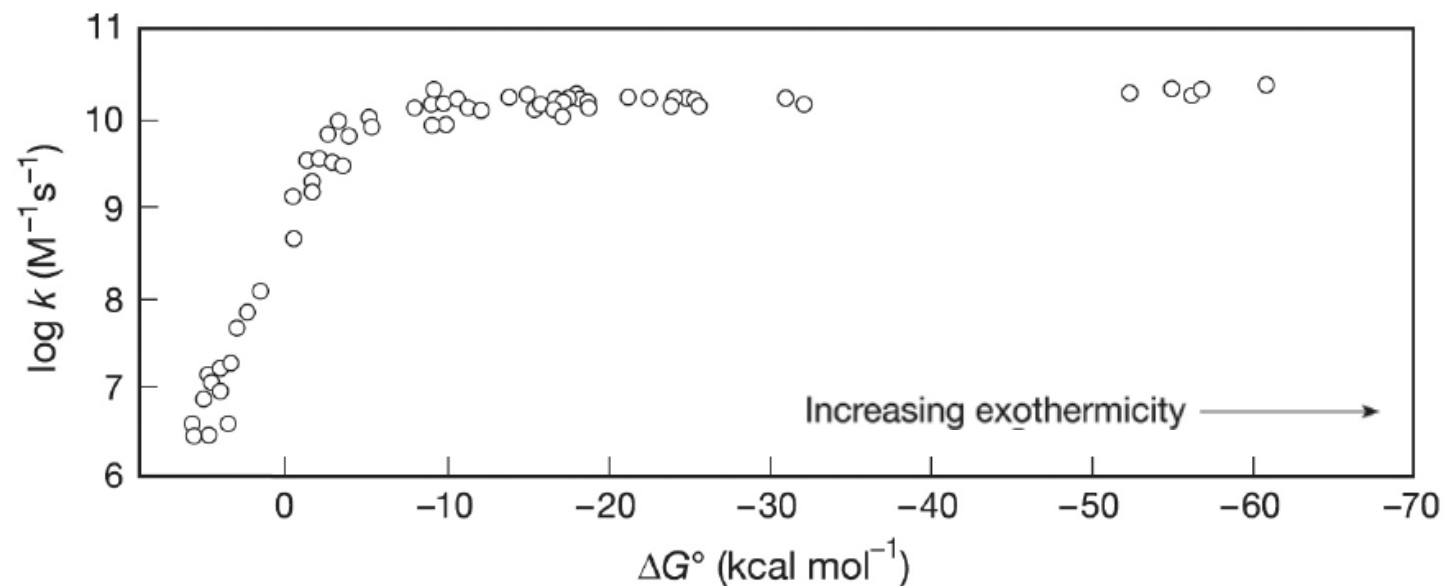


### Donors

Naphthalene\*  
 9, 10 – Dimethyl anthracene\*  
 Pyrene\*  
 Benz(a)anthracene\*  
 etc.

### Acceptors

Pyrene -3 -carboxylic acid  
 Benz(c)actidine  
 Benz(a) anthracene  
 Pyrene-4-carboxylic  
 etc.



The quenching rate seems to be saturating even though the driving force is increased. Since the saturation value is at  $k_{diff} \approx 2 \cdot 10^{10} M^{-1} s^{-1}$  this saturation indicates diffusion limitation

## Non-radiative energy transfer processes

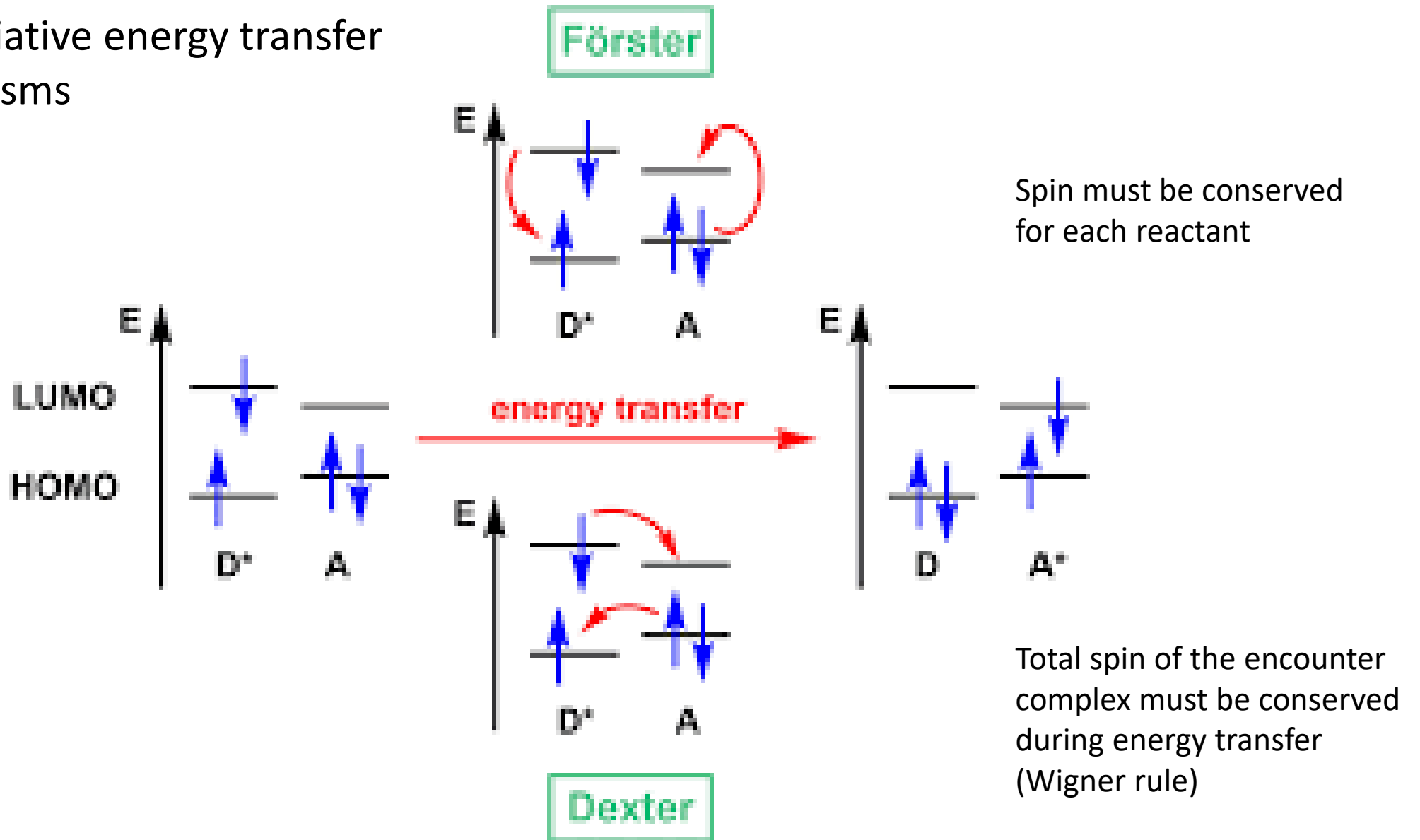
- 1) Exchange electronic energy transfer, where  $^*R$  is an energy donor, M is an energy acceptor.  $^*R + M \rightarrow R + ^*M$ , referred to as **Dexter Energy Transfer**

Interaction between  $^*D$  and A is made through *the overlap of orbitals of  $^*D$  and A*

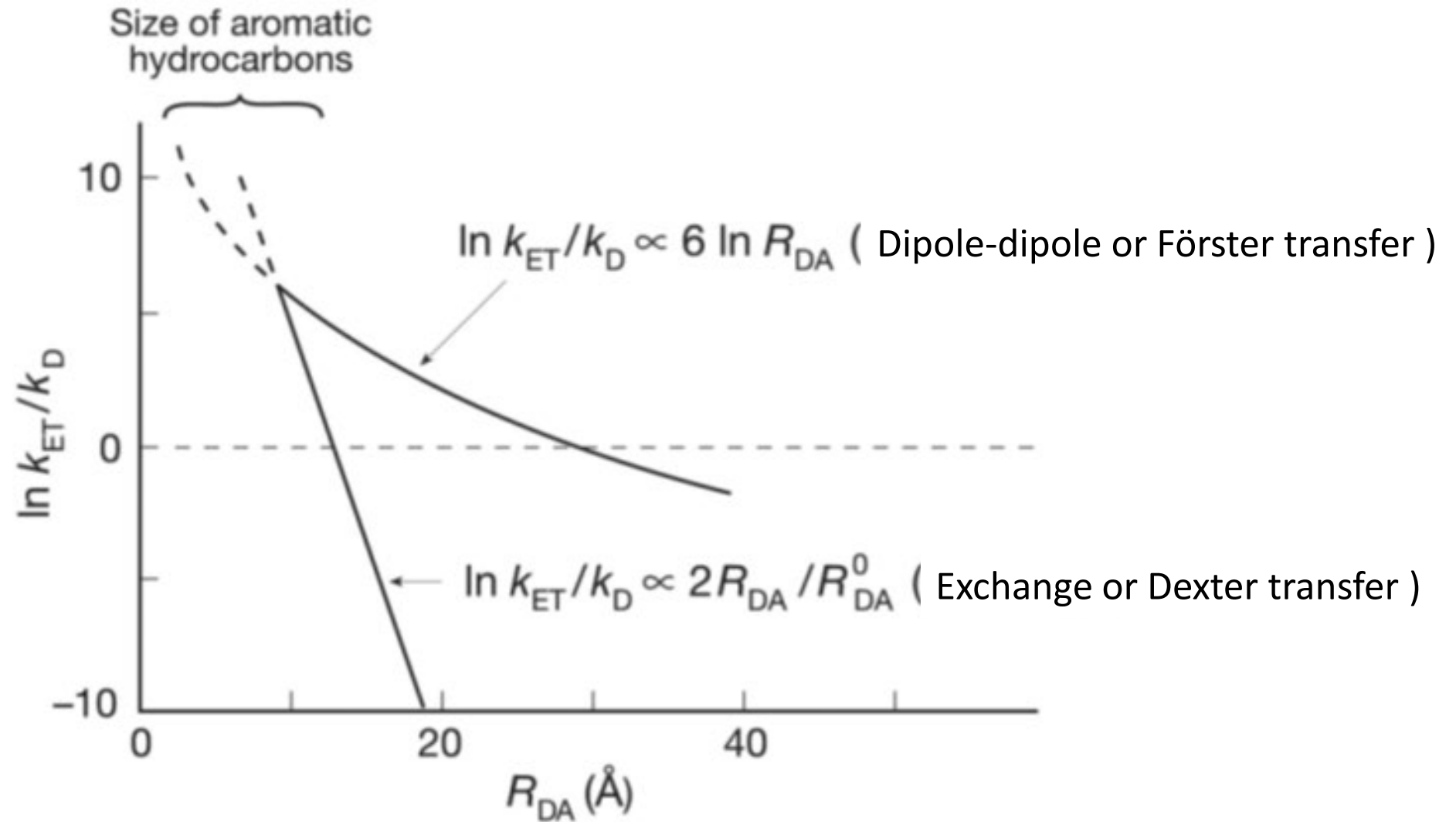
- 2) Dipole–dipole electronic energy transfer, where  $^*R$  is an energy donor, M is an energy acceptor, where  $^*R + M \rightarrow R + ^*M$ , referred to as **Förster Energy Transfer**

Interaction between  $^*D$  and A is made through space by *the overlap of the dipolar electric fields of  $^*D$  and A*

# Non-radiative energy transfer mechanisms

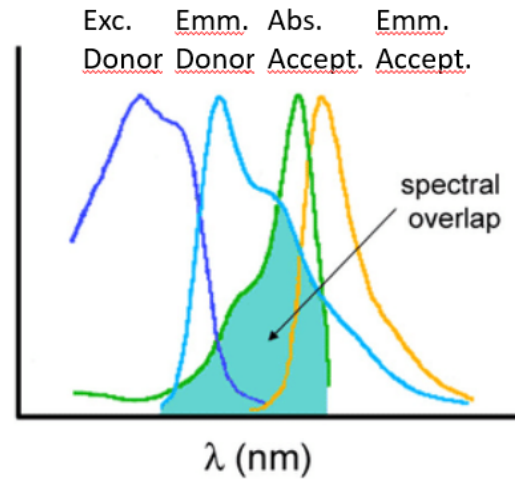
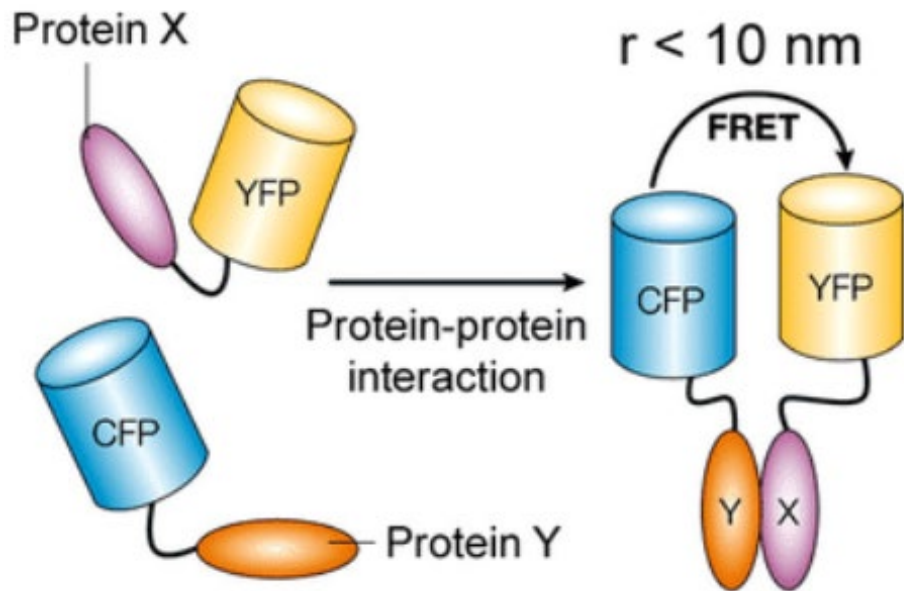


# Distance dependence of non-radiative energy transfer

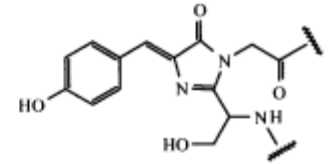


Förster resonance energy transfer (commonly termed **FRET**) is widely used in photobiology as a ruler to determine distances between chromophores, sometimes strategically placed to examine special features or conformations of molecules

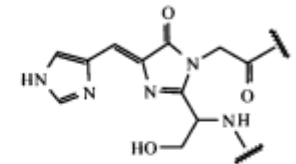
CFP: cyan fluorescent protein  
 YFP: yellow fluorescent protein



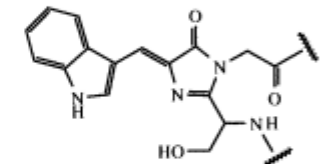
GFP



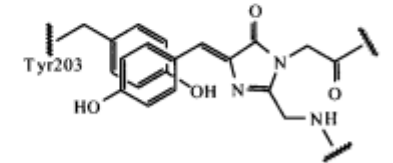
GFP-Y66H  
(BFP)



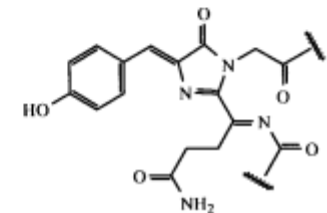
GFP-Y66W  
(CFP)



GFP-S65G/T203Y  
(YFP)

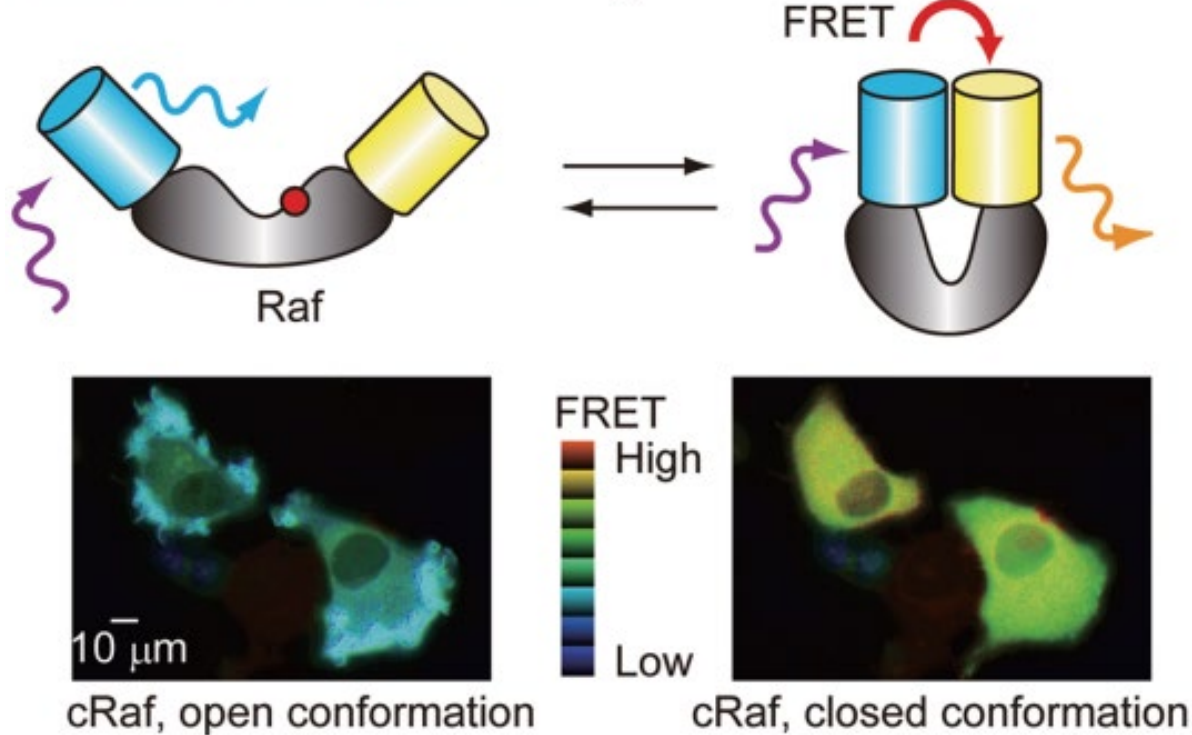


DsRED

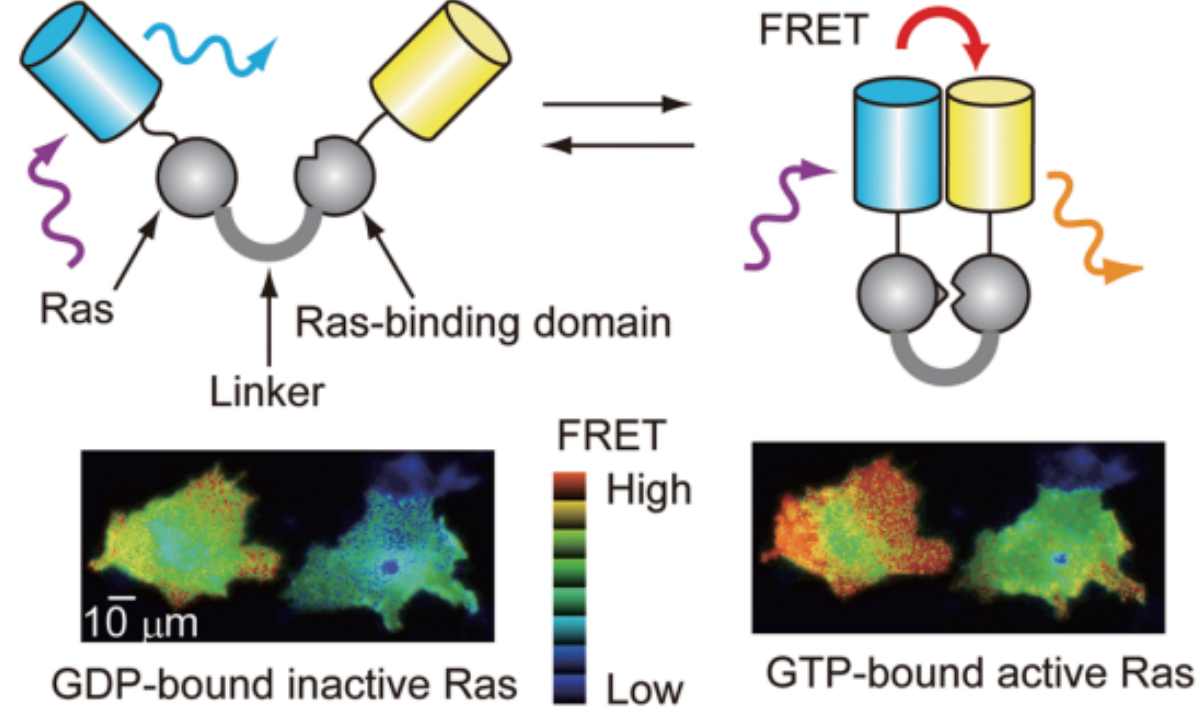


# Biosensor based on FRET

Detection of conformational change

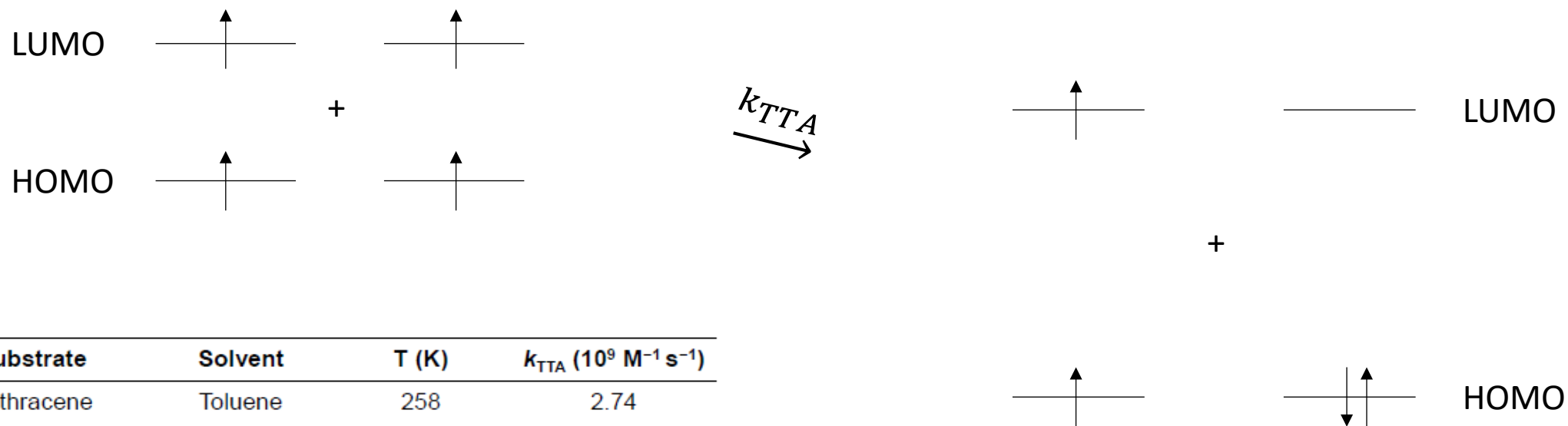
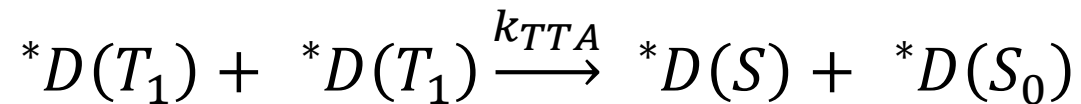


Detection of protein-protein interaction



Not only the emission intensity/spectra, but also the emission lifetime can be used in the analysis

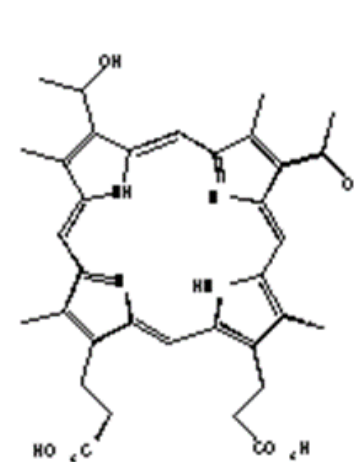
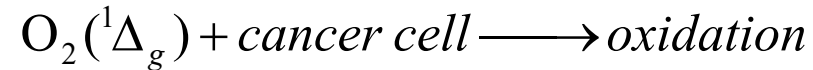
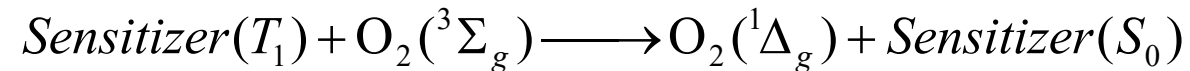
# Occurrence of Dexter energy transfer: Triplet-triplet annihilation (fusion)



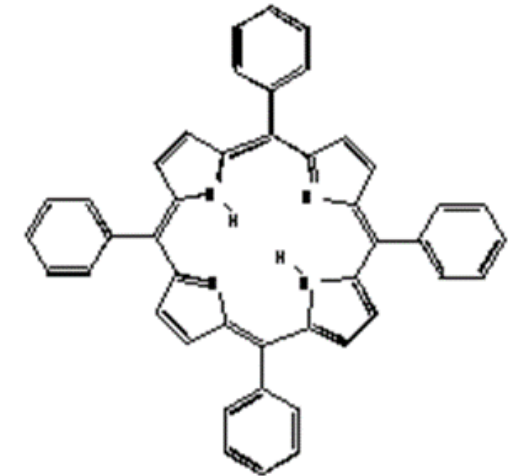
Substrate	Solvent	T (K)	$k_{TTA}$ ( $10^9 \text{ M}^{-1} \text{ s}^{-1}$ )
Anthracene	Toluene	258	2.74
Anthracene	Toluene	298	4.10
1,2-Benzanthracene	<i>n</i> -Hexane	296	20.3
Pyrene	Cyclohexane	Room T	$7 \pm 2$
Pyrene	Dodecane	Room T	$5 \pm 1$
Pyrene	Hexadecane	Room T	$1.9 \pm 0.2$

# Photodynamic therapy (Dexter Exchange)

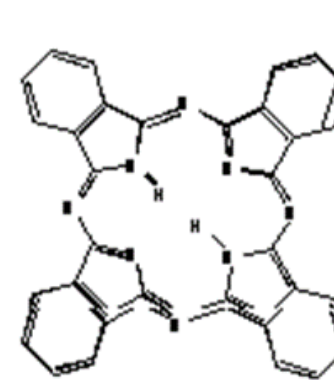
Photodynamic therapy is a two-stage treatment that combines light energy with a medicine called a photosensitizer. The photosensitizer kills cancerous and precancerous cells when activated by light, usually from a laser. The photosensitizer is nontoxic until it is activated by light.



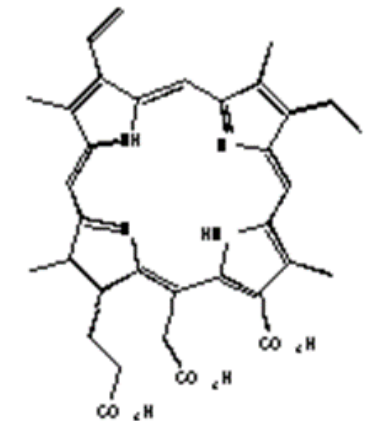
Haematoporphyrin



Meso tetraphenylporphyrin

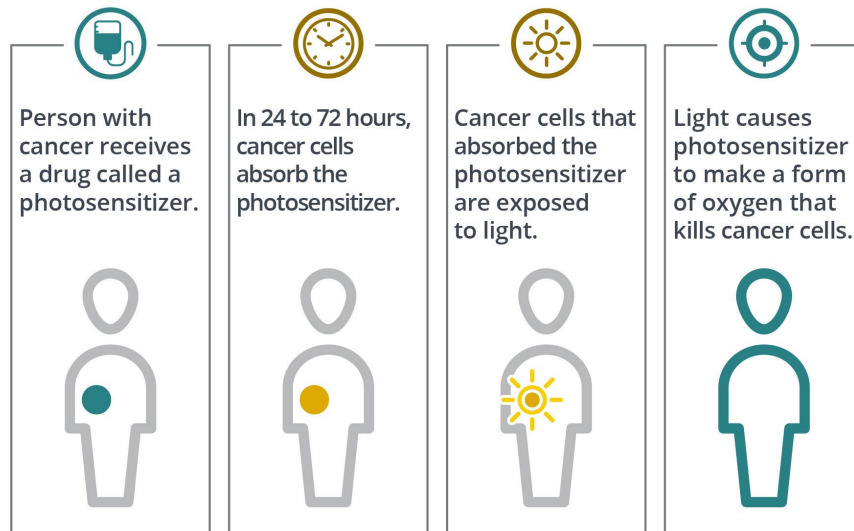


Phthalocyanine

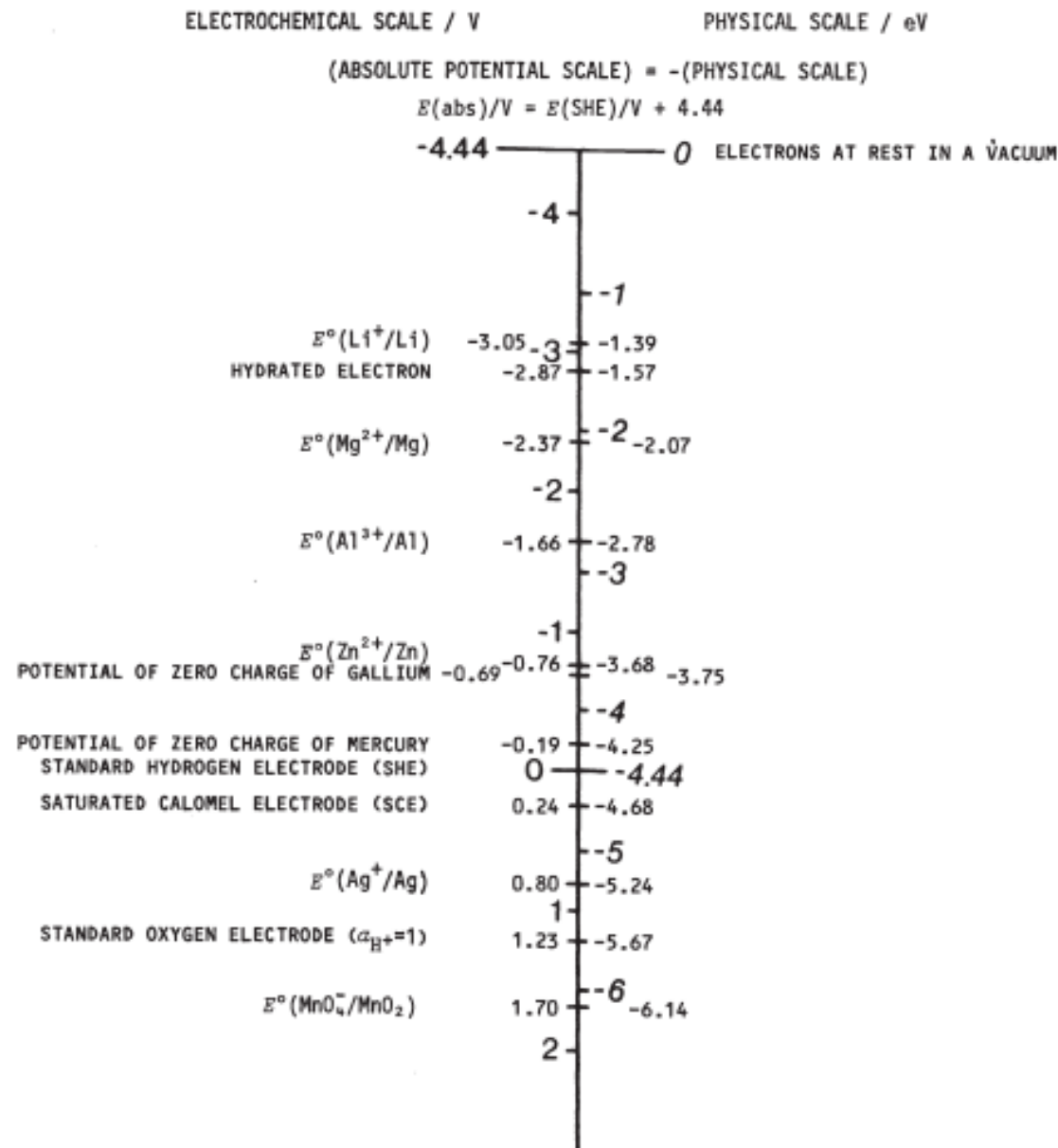
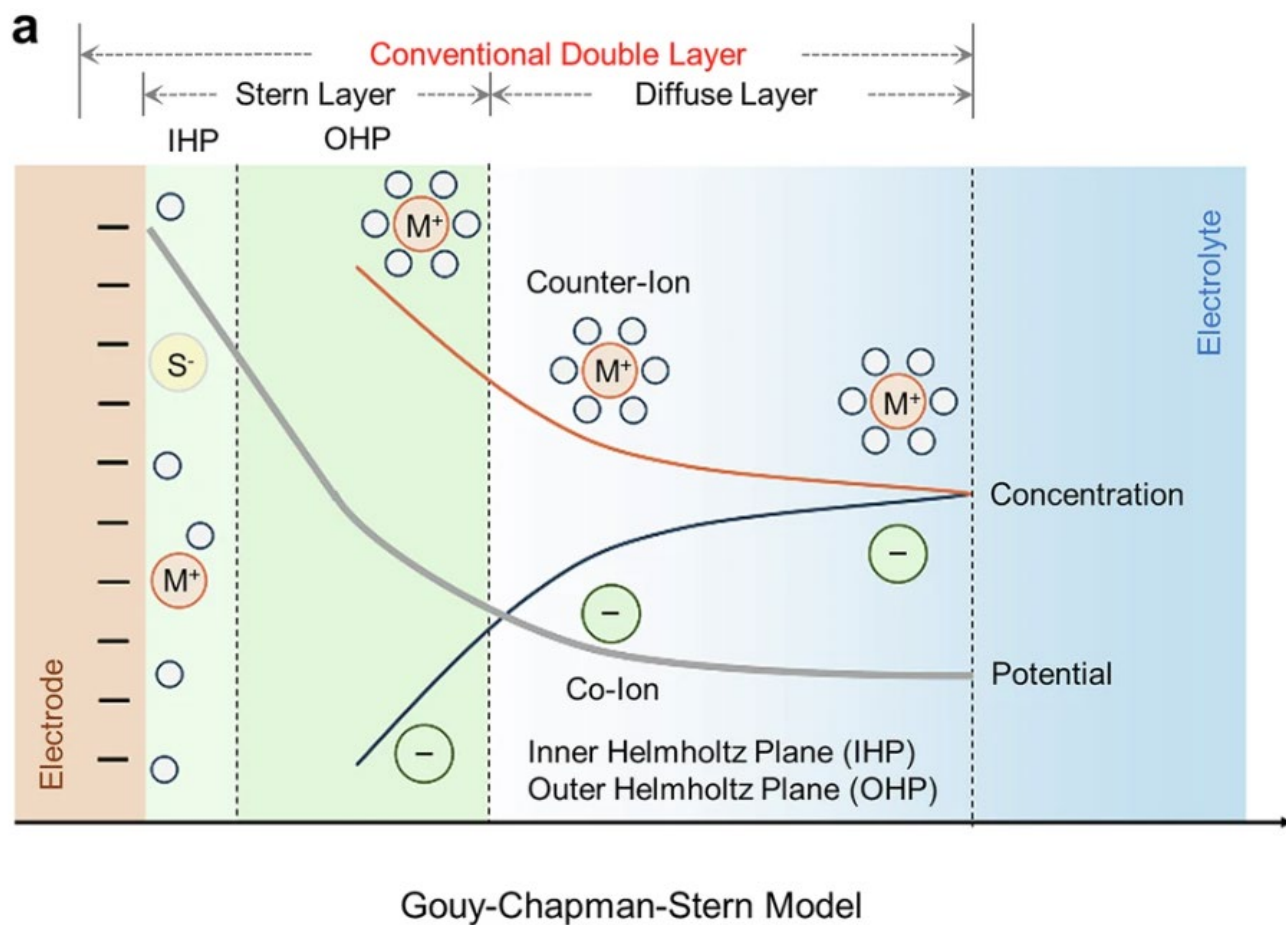


Chlorin

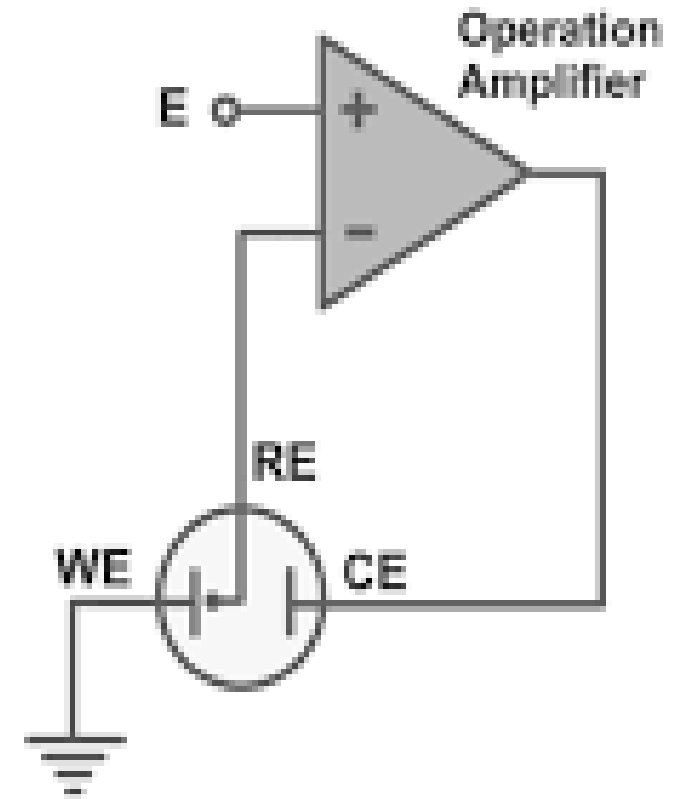
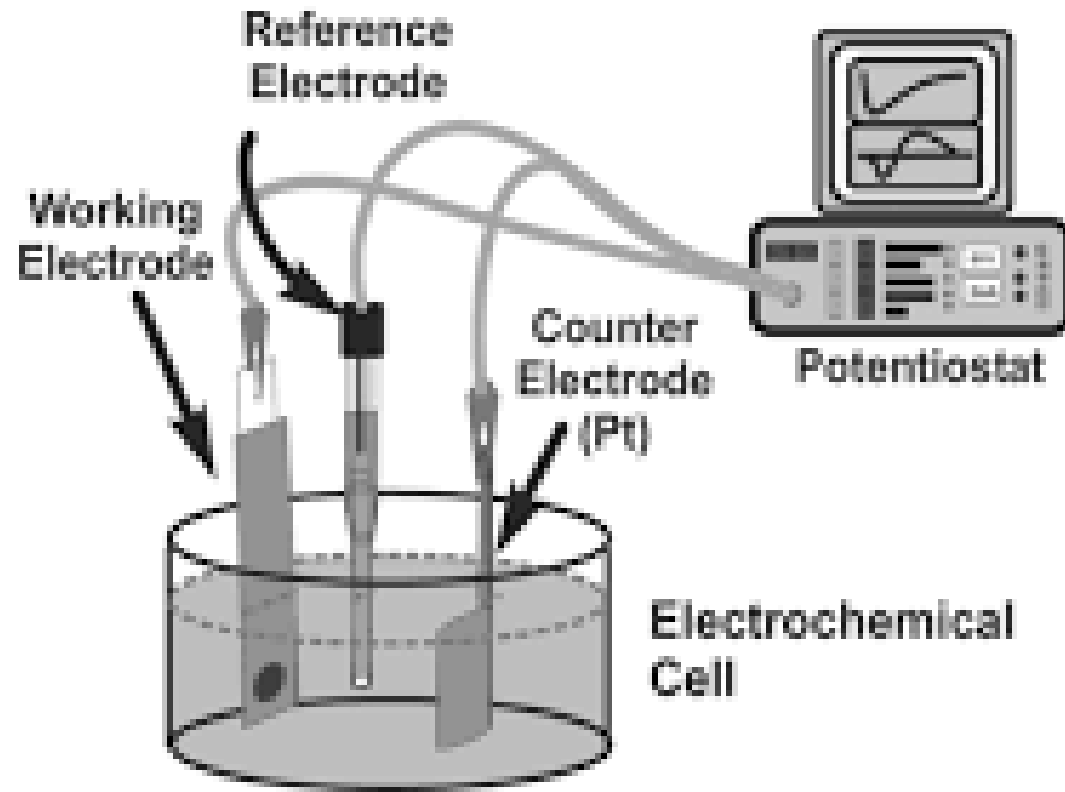
## PHOTODYNAMIC THERAPY



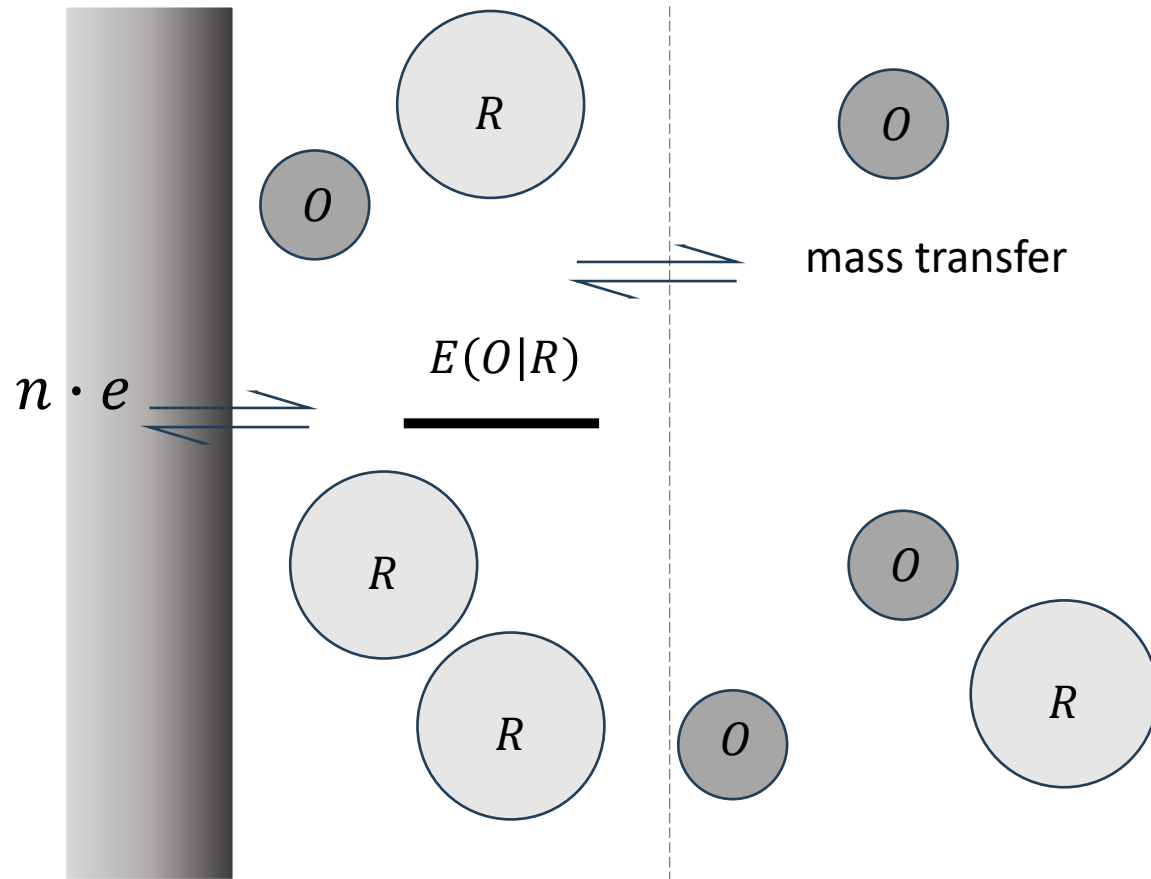
# Electrochemical reactions



# Three electrode electrochemical cell



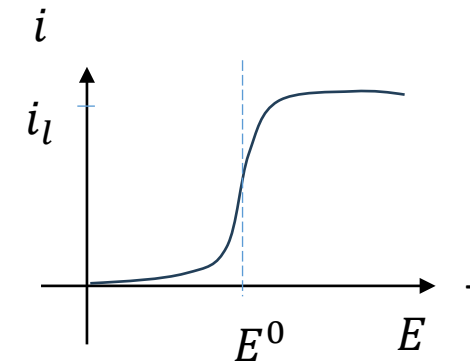
# Mass transfer limited kinetics of electrode reactions



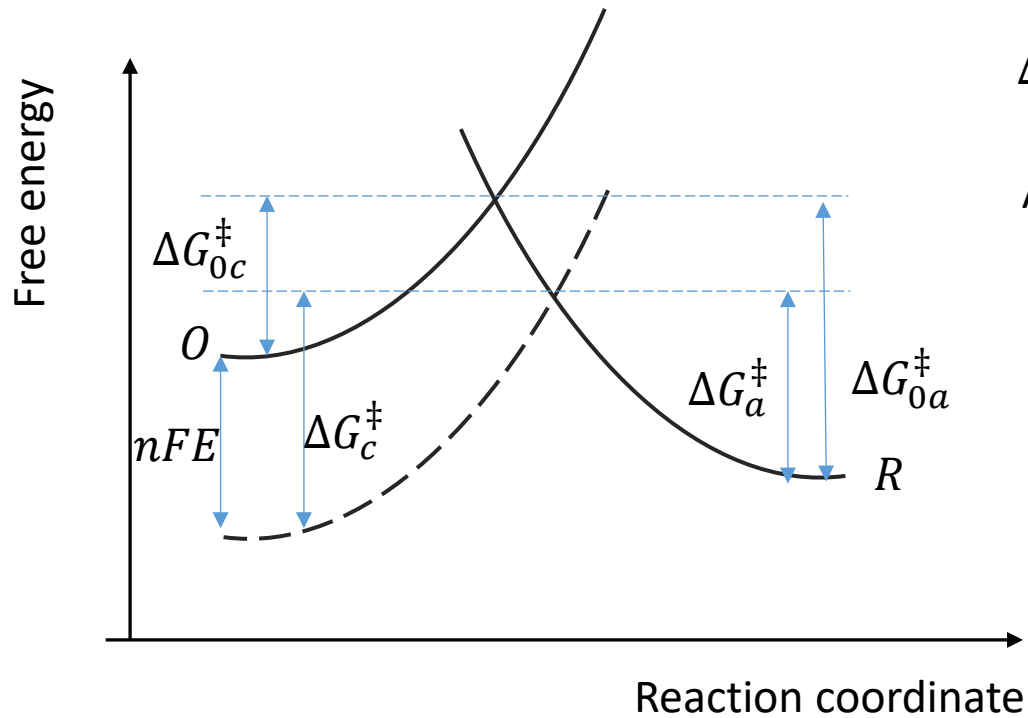
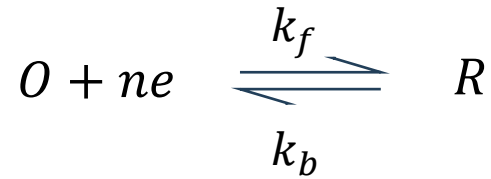
$$E(O|R) = E^0 + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$

Nernst equation: rapid exchange kinetics

$$E(O|R) = E^0 + \frac{RT}{nF} \ln \frac{i_l - i}{i}$$



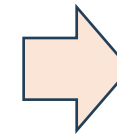
# Kinetics of electrode reactions



The values of  $k_f$  and  $k_b$  depend on the applied electrode potential  $E$

$$\Delta G_c^\ddagger = G_{0c}^\ddagger + \alpha nFE$$

$$\Delta G_a^\ddagger = G_{0a}^\ddagger - (1 - \alpha)nFE$$



$$k_f = A_f e^{-\Delta G_c^\ddagger/RT}$$

$$k_b = A_b e^{-\Delta G_a^\ddagger/RT}$$

At equilibrium:  $k_f C_O = k_b C_R$  and we can write

$$k_f = k_f^0 e^{-\alpha nFE/RT}$$

$$k_b = k_b^0 e^{(1-\alpha)nFE/RT}$$

At the standard redox potential  $E^0$  we have  $C_O = C_R$  we have

$$k_f = k_b = k_0 \quad \text{(standard rate constant)}$$

$$k_f = k_0 = k_f^0 e^{-\alpha nFE^0/RT}$$

$$k_b = k_0 = k_b^0 e^{(1-\alpha)nFE^0/RT}$$

Therefore we can write:

$$k_f = k_0 e^{-\alpha nF(E-E^0)/RT}$$

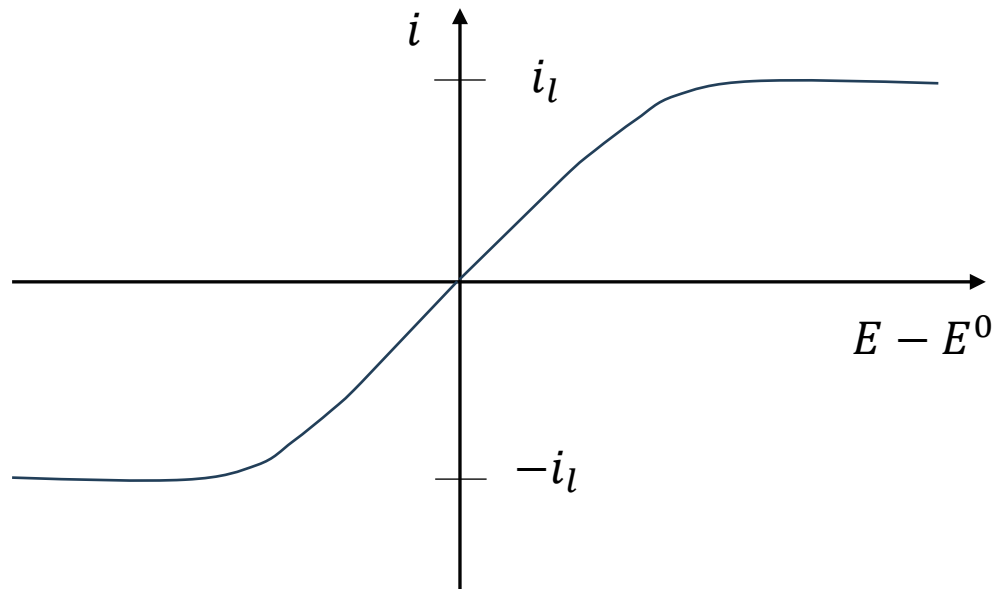
$$k_b = k_0 e^{(1-\alpha)nF(E-E^0)/RT}$$

$$i = i_c - i_a$$

$$= nFAk_0 \left[ C_0 e^{-\alpha nF(E-E^0)/RT} - C_R e^{(1-\alpha)nF(E-E^0)/RT} \right]$$

(Butler-Volmer equation)

$k_0$  is a measure of the electron transfer rate constant from the electrode to the redox couple and vice versa.



At equilibrium conditions  $i_c = i_a$  and the net current  $i = 0$ . is the electrode to the redox couple and vice versa.

$$nFAk_0 C_0 e^{-\alpha nF(E-E^0)/RT} = nFAk_0 C_R e^{(1-\alpha)nF(E-E^0)/RT}$$

This is equivalent to the Nernst equation:

$$\frac{C_0}{C_R} = e^{\frac{(1-\alpha)nF(E-E^0)}{RT} + \alpha nF(E-E^0)/RT} = e^{nF(E-E^0)/RT}$$

One can define the *exchange current*  $i_0$ , which flows back and forth from the redox couples to the electrode (one can start from O or R species):

$$i_0 = nFAk_0 C_0 e^{-\alpha nF(E-E^0)/RT}$$

For  $C_0 = C_R = C$  we can show that :

$$i_0 = nFAk_0 C$$

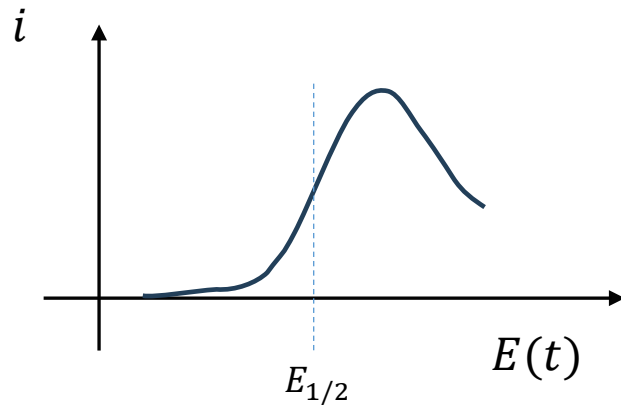
# Cyclic voltammetry

The potential is swept linearly at rate  $v$  in V/sec:

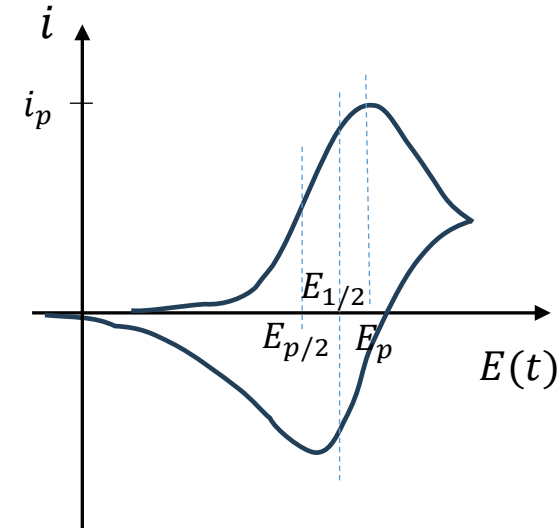
$$E(t) = E_i - vt$$

$$\frac{C_O(0,t)}{C_R(0,t)} = f(t) = e^{nF(E_i - vt - E^0)/RT}$$

This situation is different from the previous one described at constant potential. Mass transport with the diffusion of O and R comes into play.



By reversing the sweep direction one obtains a cyclic voltammogram:



Assuming that the electrode reactions are at equilibrium and starting from oxidized species only, one can show that:

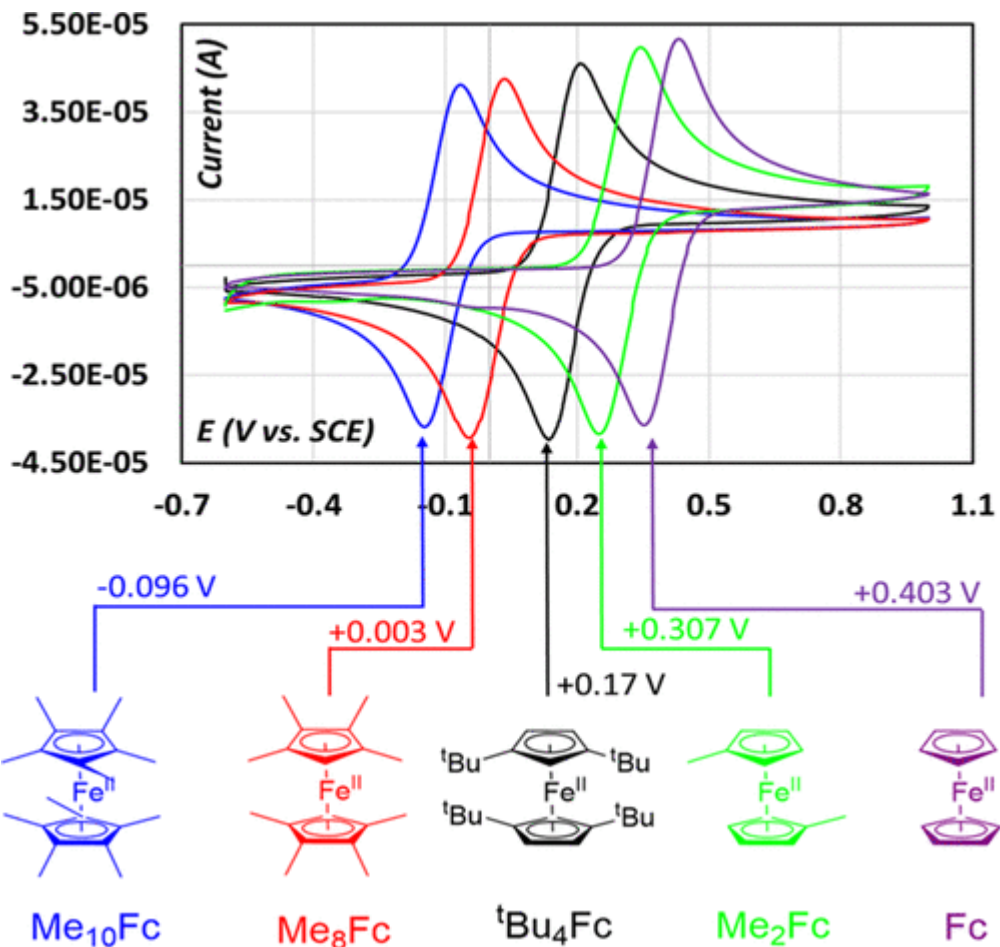
$$i = (2.69 \cdot 10^5) \cdot n^{3/2} AD_0^{1/2} v^{1/2} C_O$$

and

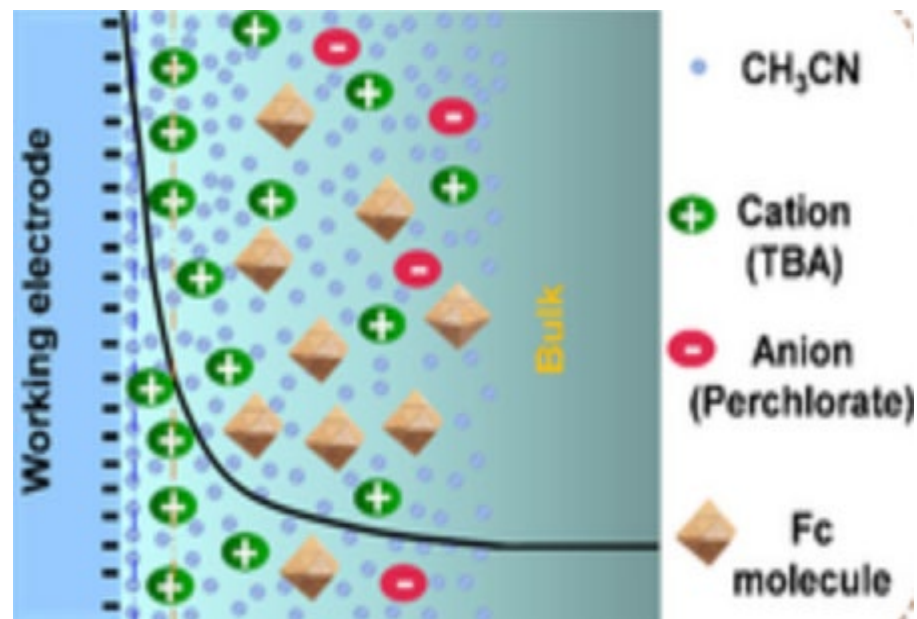
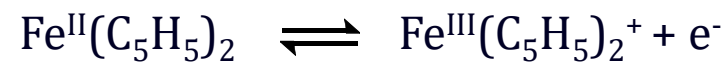
$$E_p - E_{1/2} = -1.09 \left( \frac{RT}{nF} \right)$$

Note: for a perfectly reversible system  $E_{1/2} = E^0$

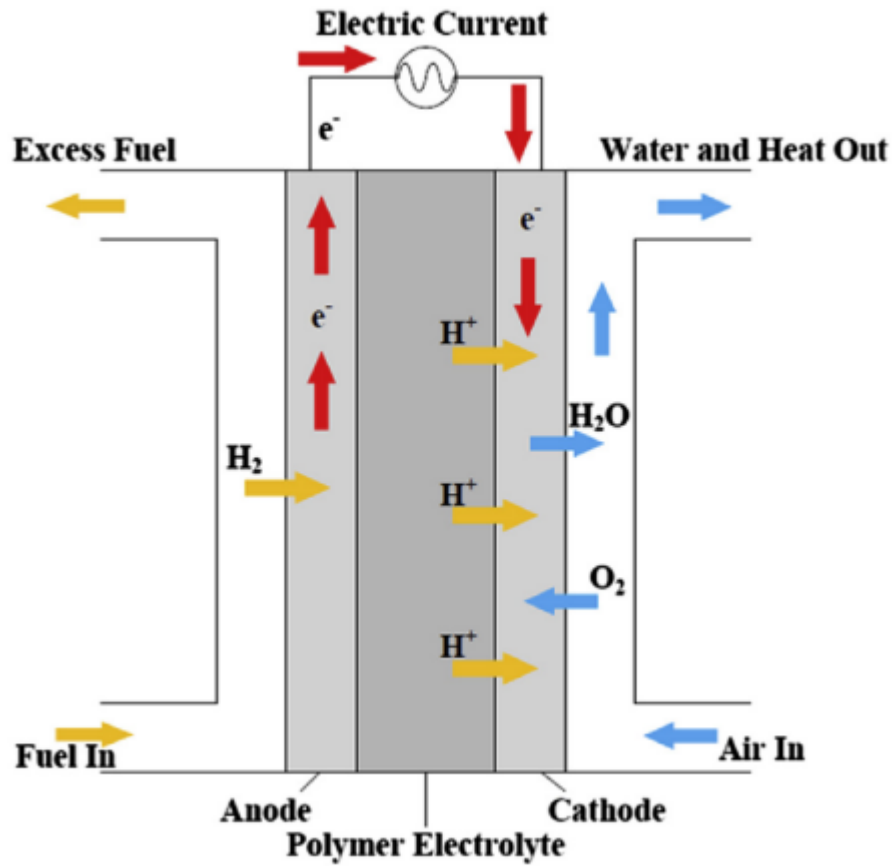
# Cyclic voltammetry (in general mass transport limited kinetics)



Oxidation of ferrocene,  $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5)_2$ , to the ferrocenium cation,  $\text{Fe}^{\text{III}}(\text{C}_5\text{H}_5)_2^+$  and corresponding reduction:

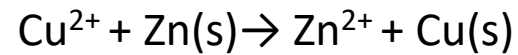
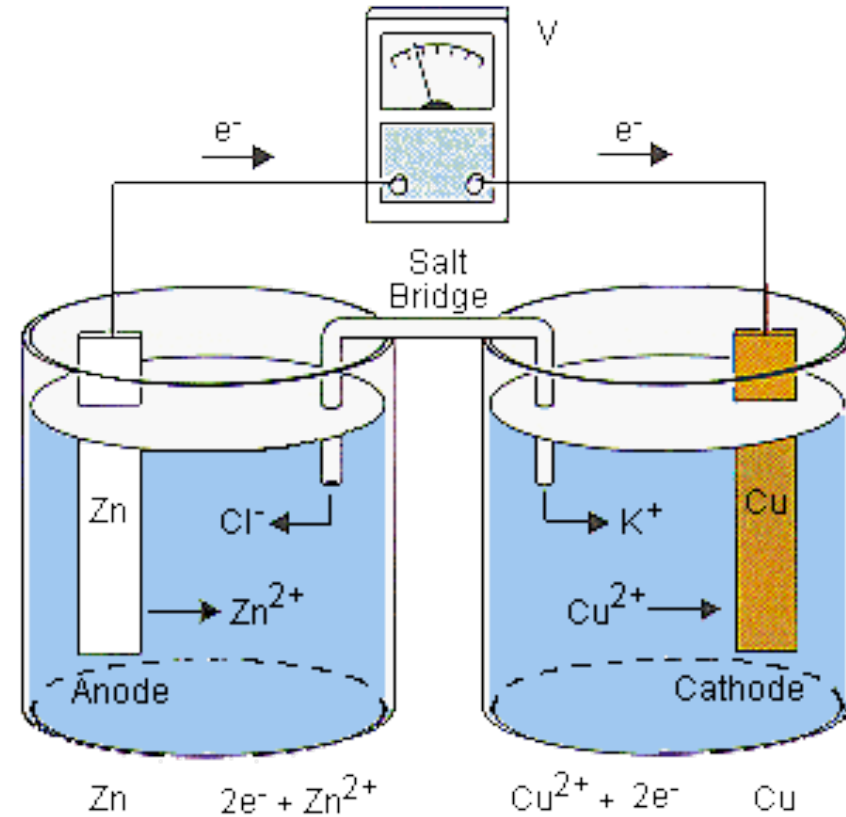


## Fuel cells:



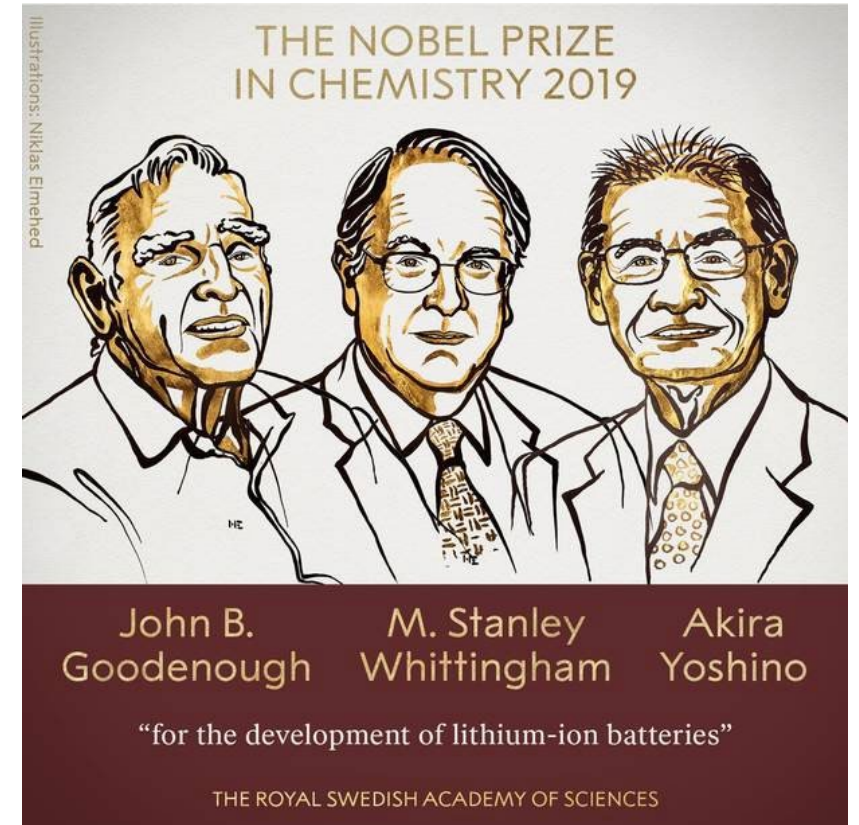
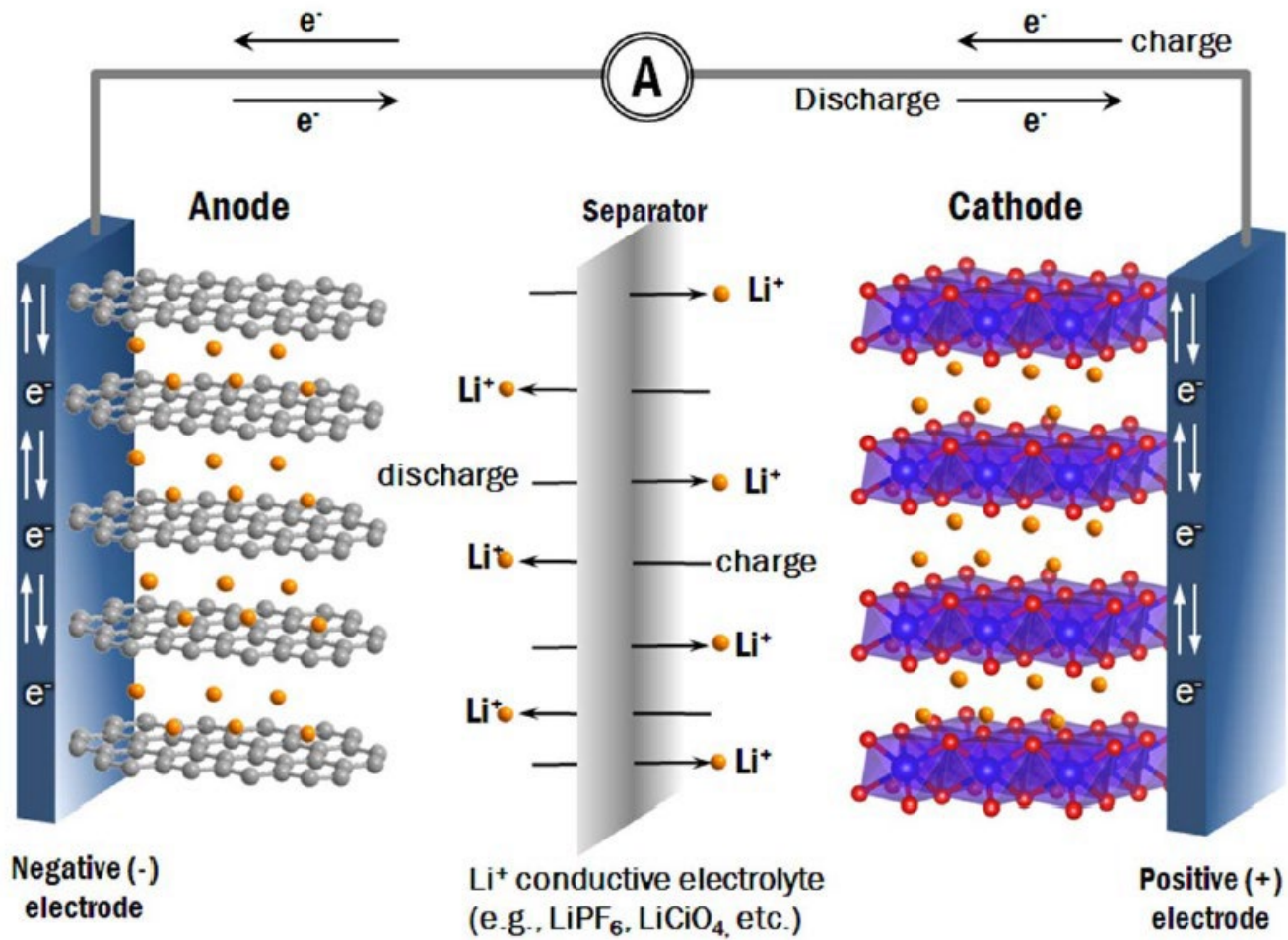
## Batteries:

### Copper-Zinc battery

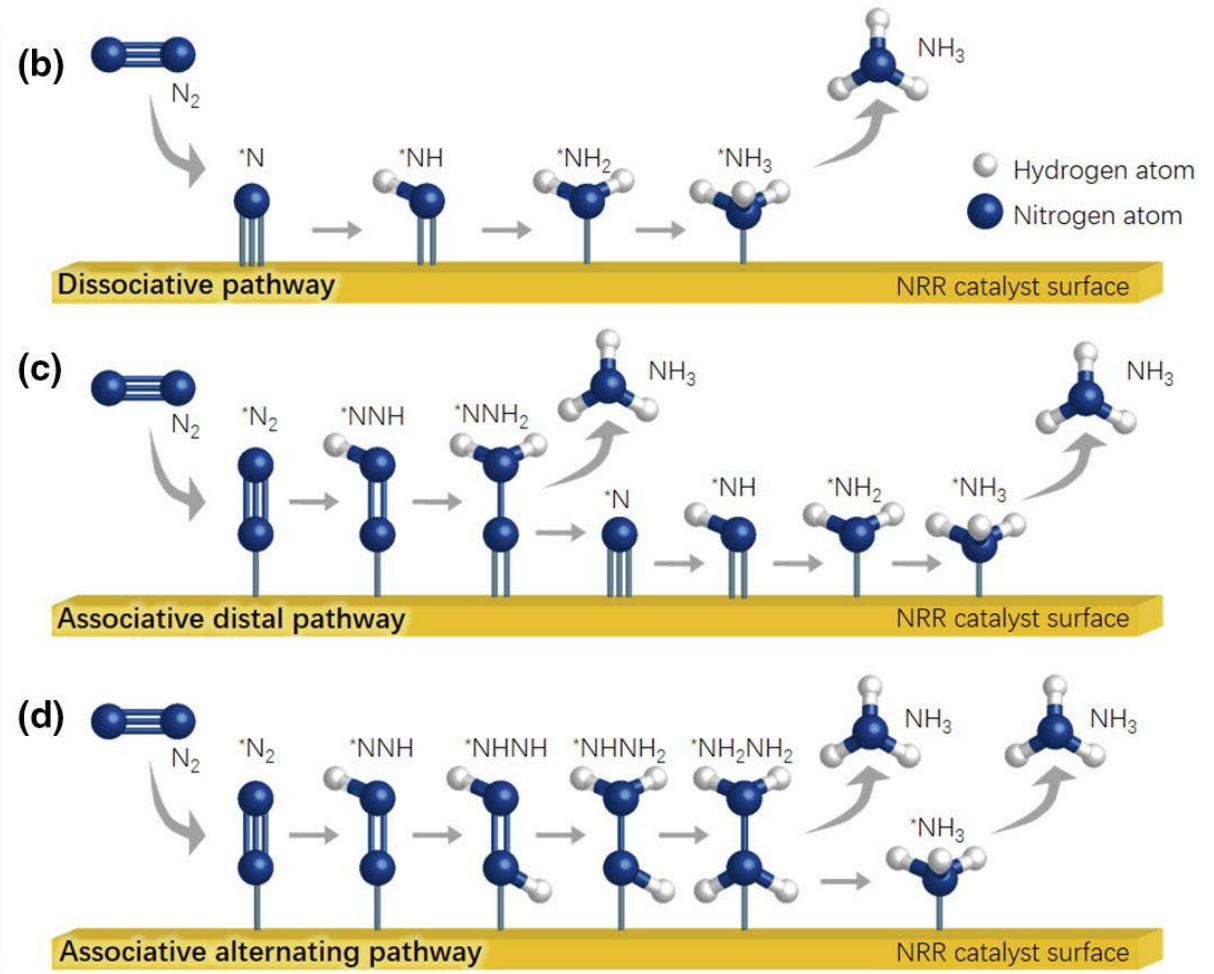
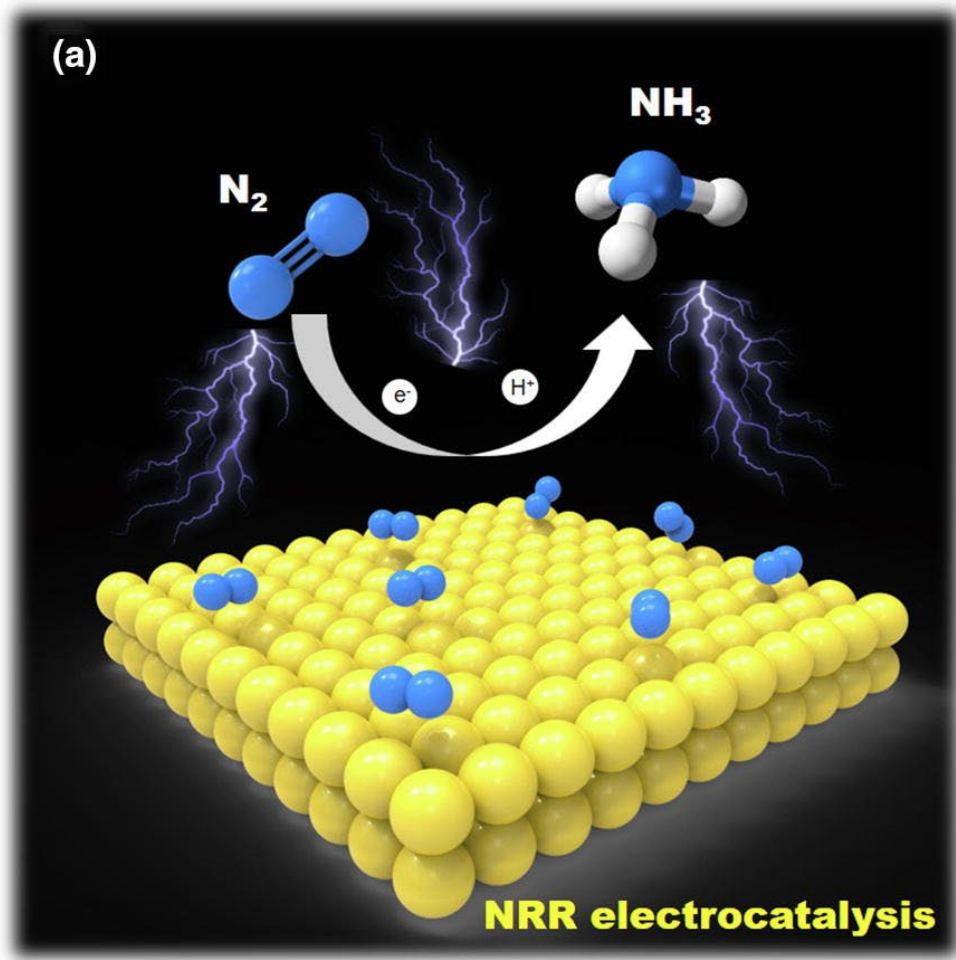


Standard-State Reduction Half-Cell Potentials

# Li-ion batteries:



# Electron transfer in heterocatalysis



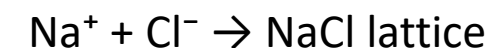
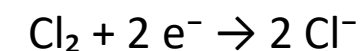
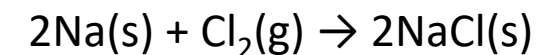
# Chemical reactions

Redox processes are defined as reactions accompanied by oxidation-state changes: an increase in an atom's oxidation number corresponds to an oxidation; a decrease, to a reduction.

Group (vertical)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period (horizontal)																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.291		

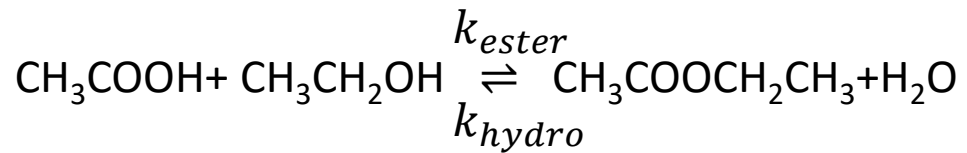
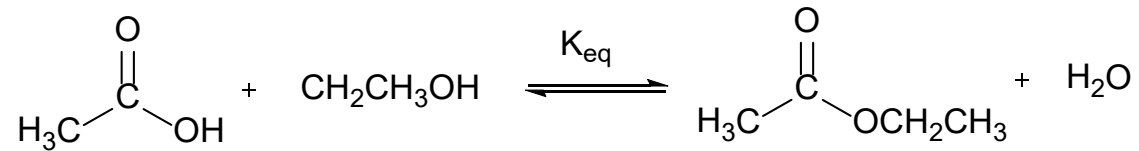
Periodic table of electronegativity using the Pauling scale

Example:



# Chemical equilibrium

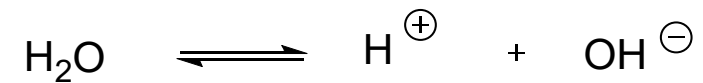
Esterification, hydrolysis reaction:



$$K_{\text{eq}} = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]} = 4 = \frac{k_{\text{ester}}}{k_{\text{hydro}}}$$

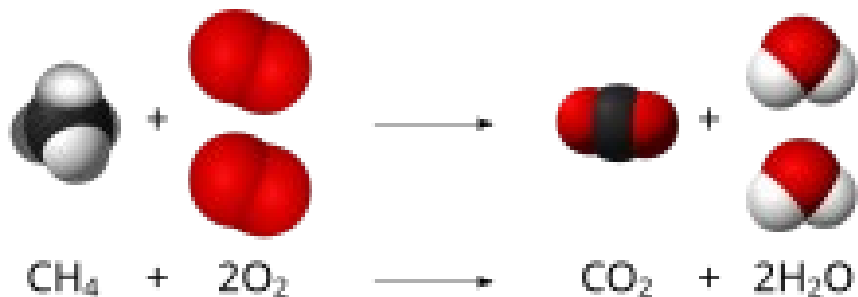
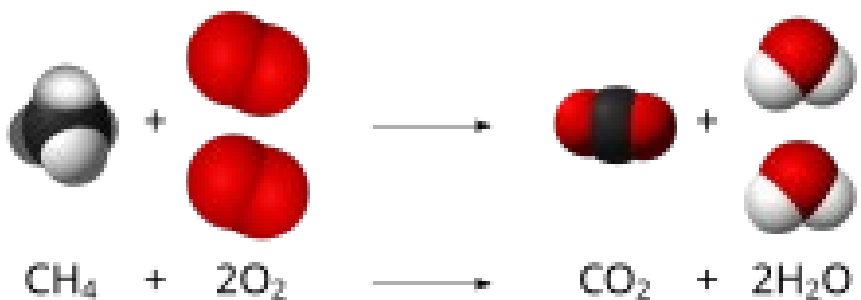
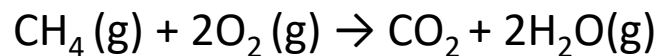
$$\Delta G_{\text{ester}}^\theta = -RT \ln 4 = -3435 \text{ J mol}^{-1}$$

Autoionization of water:

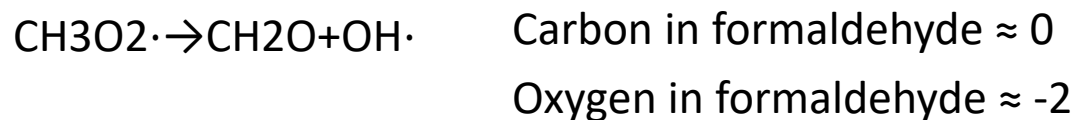
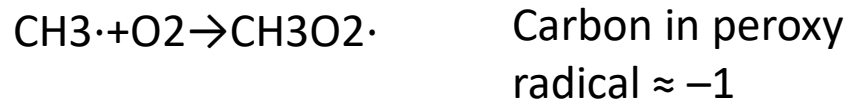


$$K_W = [\text{H}^+][\text{OH}^-] = 10^{-14} = \frac{k_{\text{ionization}}}{k_{\text{recombination}}}$$

# Combustion reactions



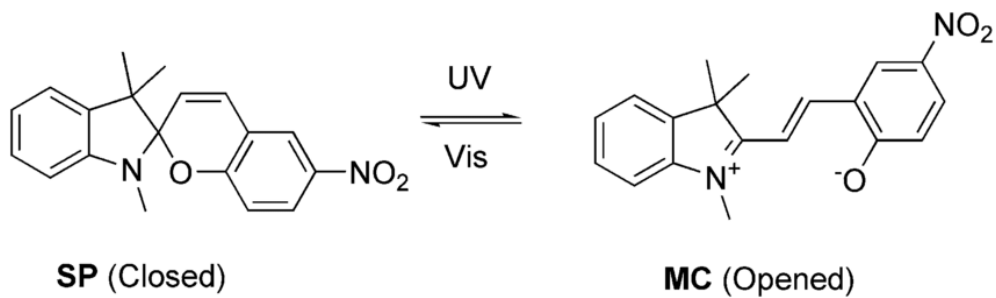
Hydrogen abstraction



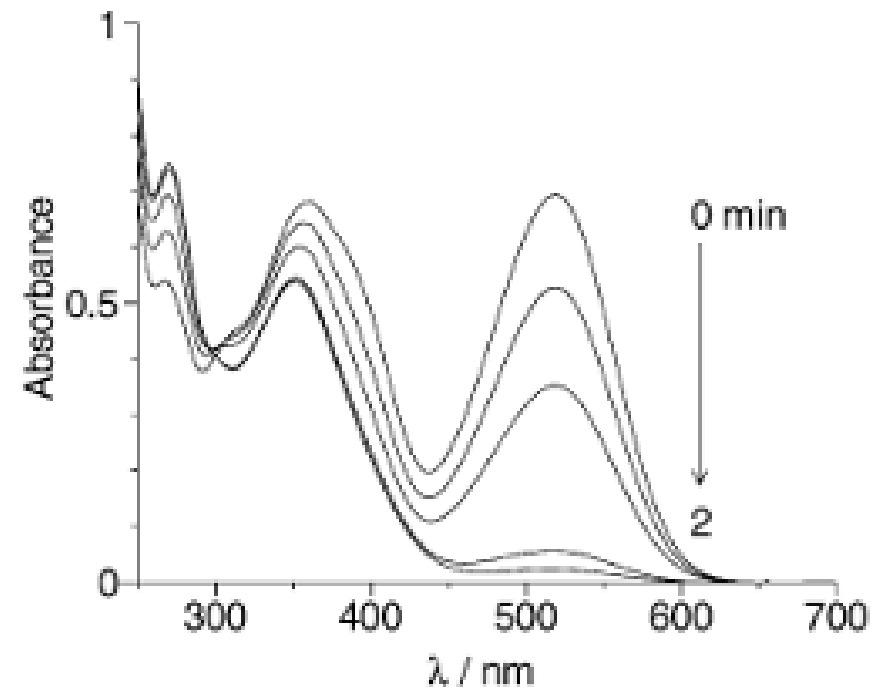
Carbon has lost **8 electrons total**

Oxygen has gained those electrons **gradually across bonds**

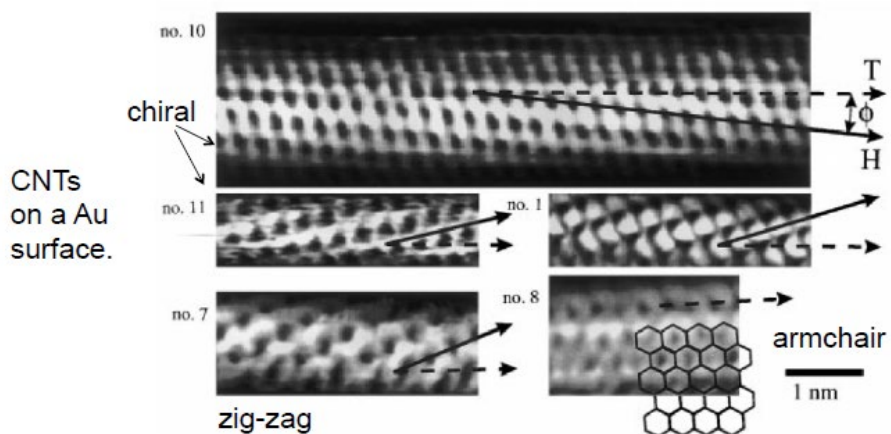
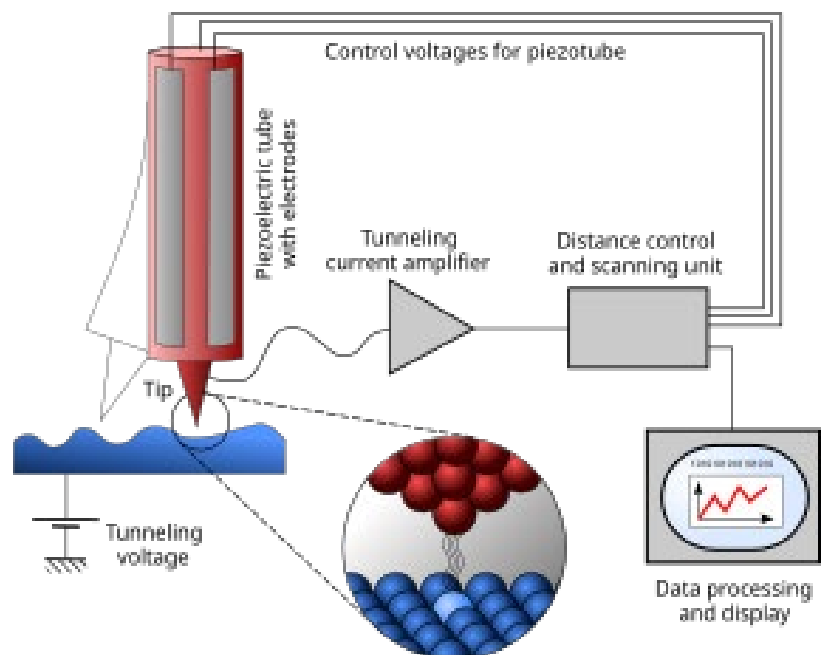
# Photoinduced Spiropyrane-Merocyanine isomerization



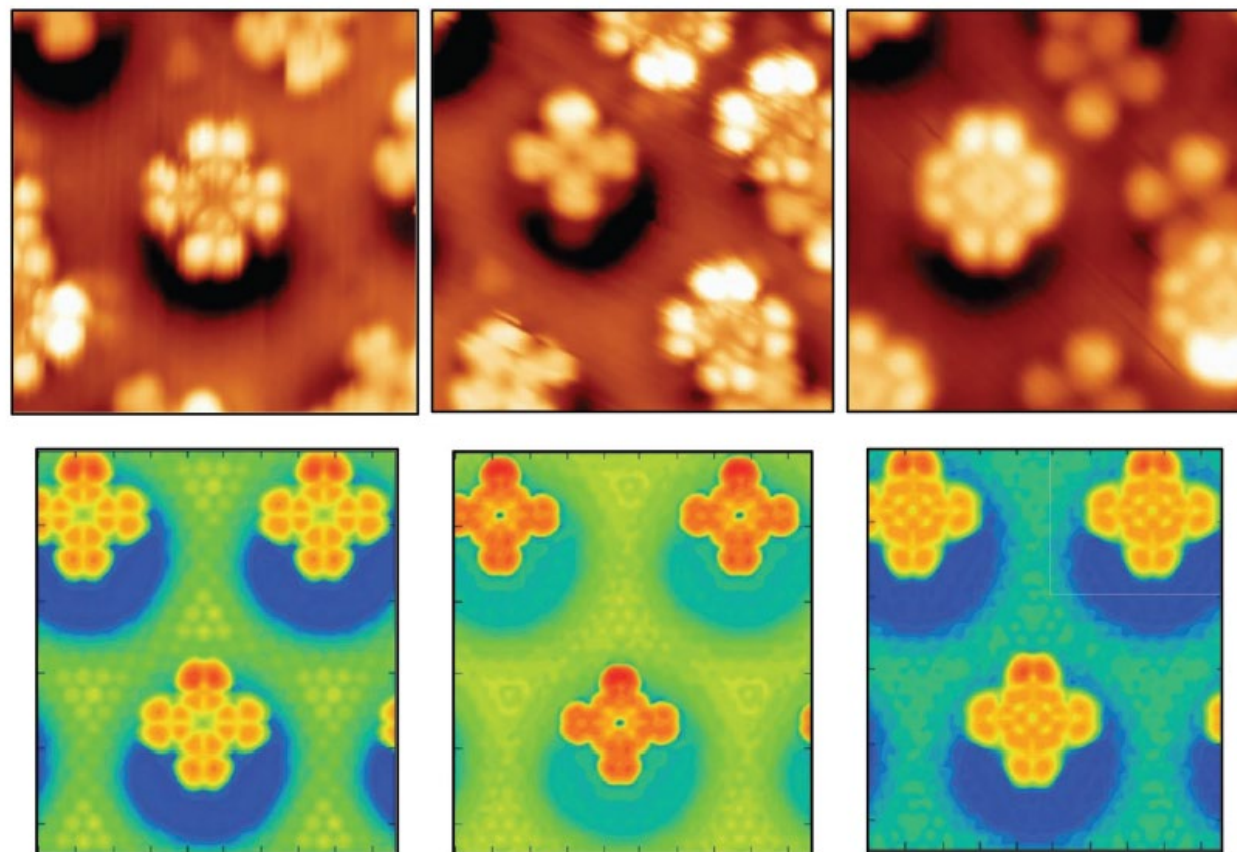
Color change upon irradiation with 500 nm light



# Measuring molecular orbitals via scanning tunneling microscopy (STM)

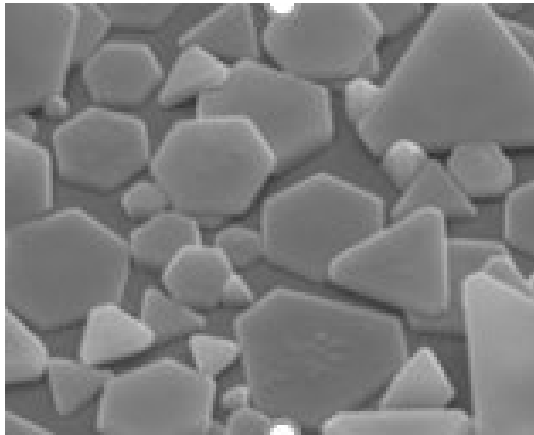


J.W.G. Wildoer, C. Dekker et al, Nature 391, 59 (1998).

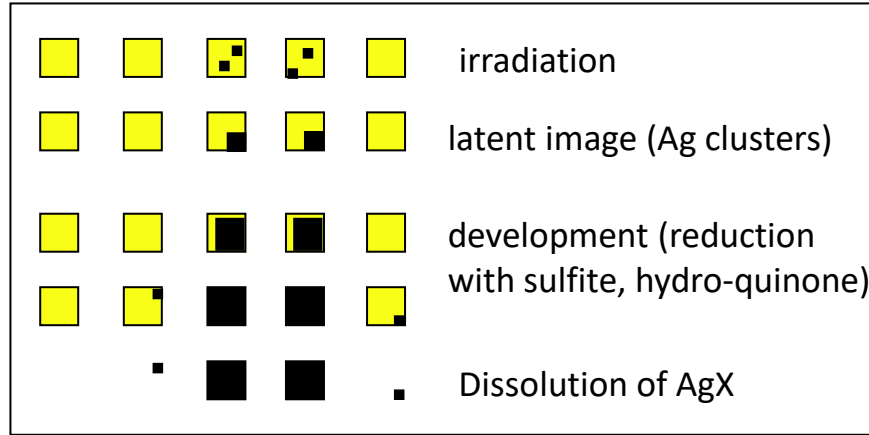


**Top panels:** experimental STM images of one phthalocyanine molecule adsorbed at an off-center pore site of a nanomesh obtained by different bias potentials. Left  $V_b = 2$  eV, middle  $V_b = 1$  eV, right  $V_b = +1$  eV. Bottom panels: simulated STM images of the offA1 optimized structure, also obtained with the same three bias potentials

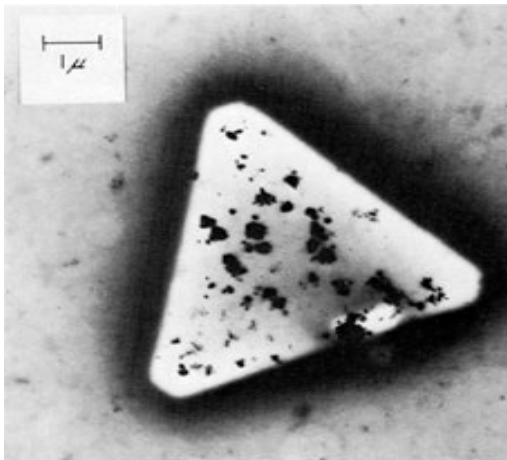
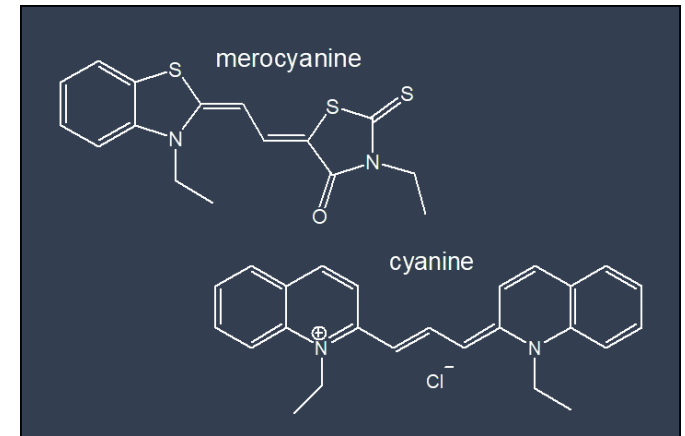
# Silver halide photography



Unexposed AgBr grains



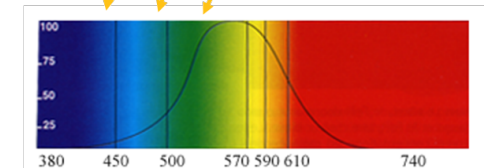
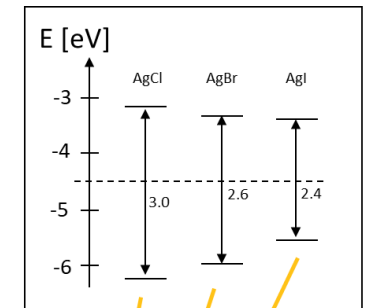
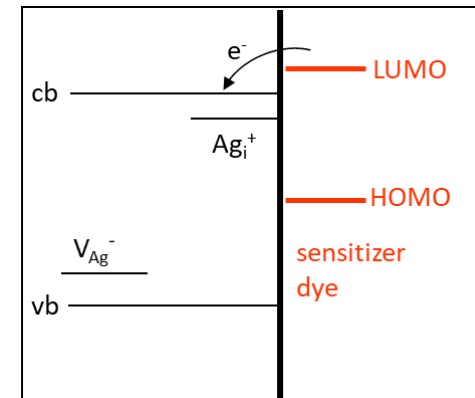
## Photographic sensitizers



After heavy irradiation

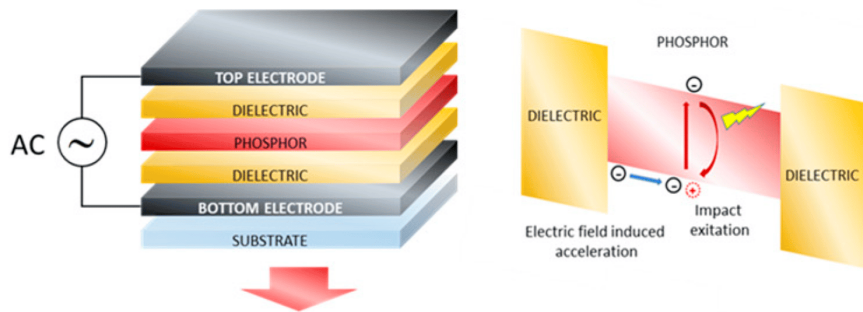


After development

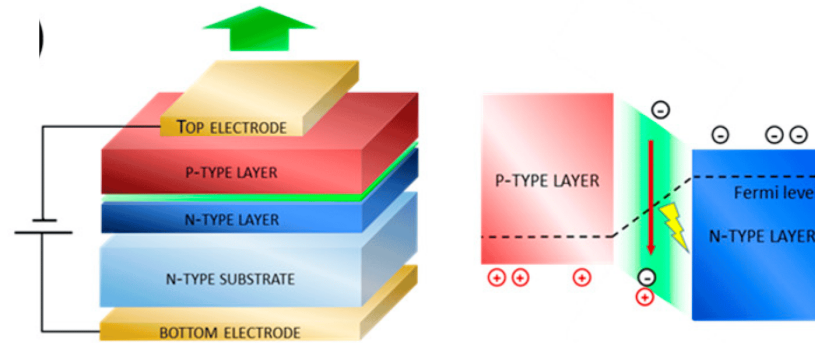


# Energy and electron transfer processes optoelectronics

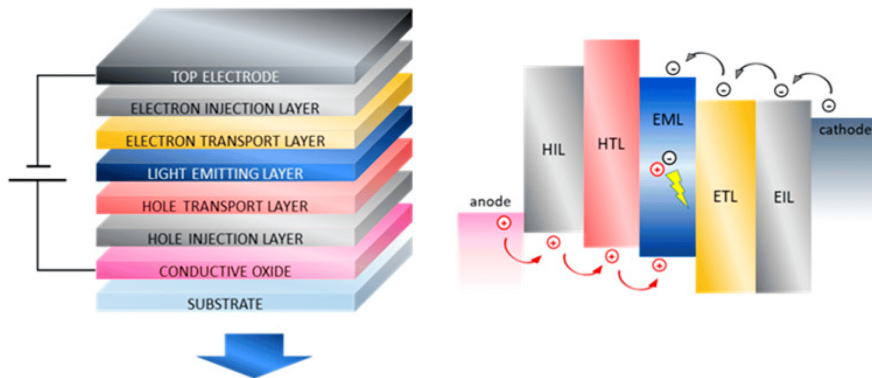
*Electroluminescence (impact)*



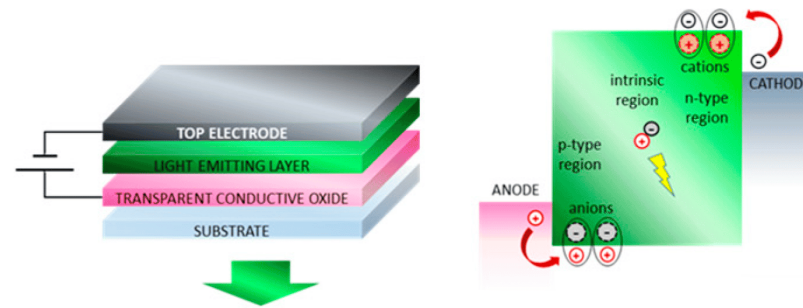
*Light-emitting diode (LED)*



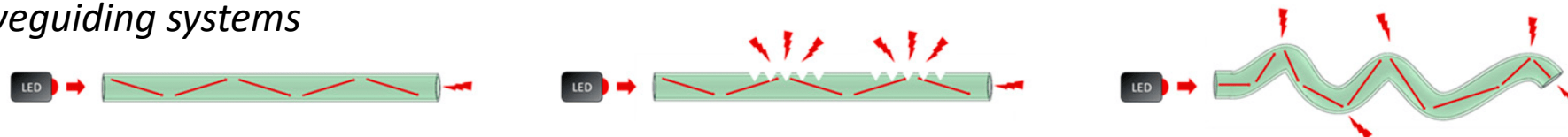
*Organic light-emitting diode(OLED)*



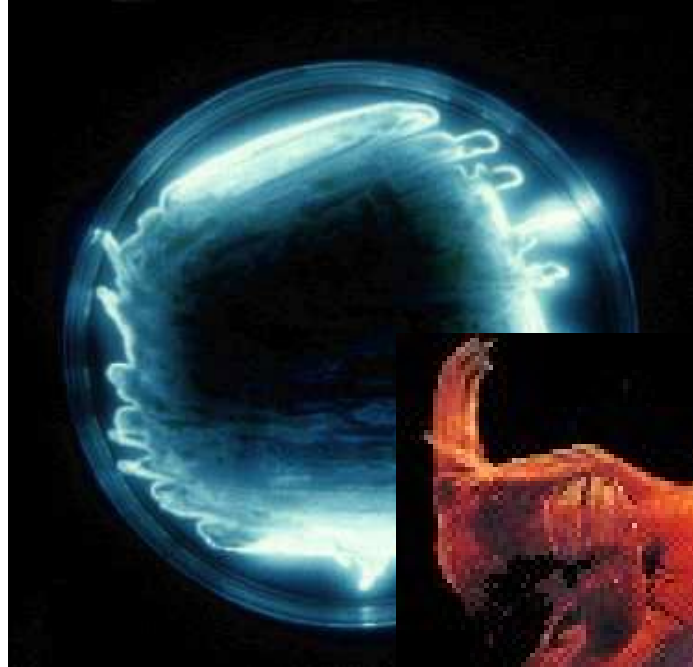
*Light-emitting electrochemical cell (LEC)*



*Waveguiding systems*



*Energy and electron transfer in biological systems*



*Photobacterium*



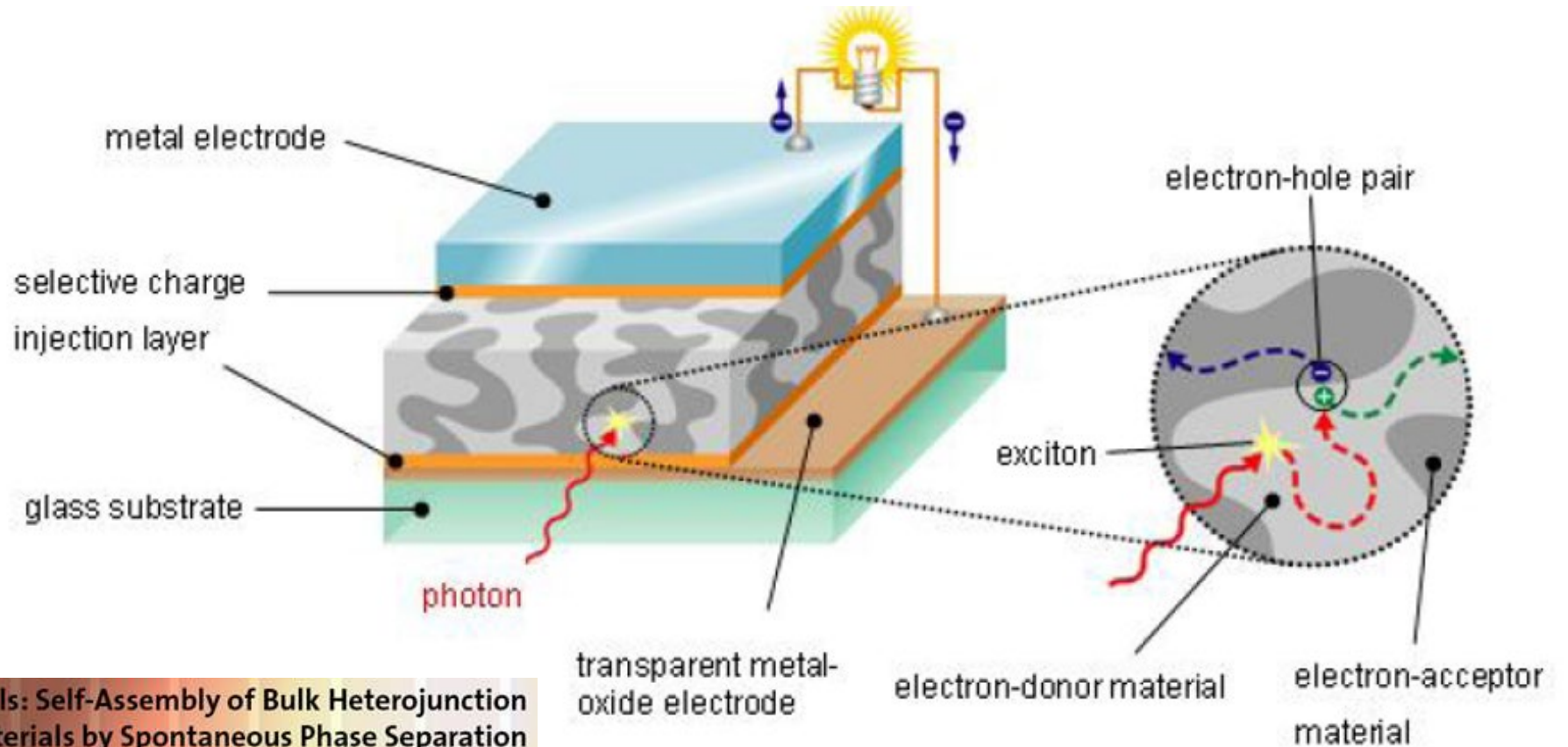
*Light-emitting organ (lure)*

*Plant photosynthesis*



*Fire fly*

# Organic photovoltaic devices



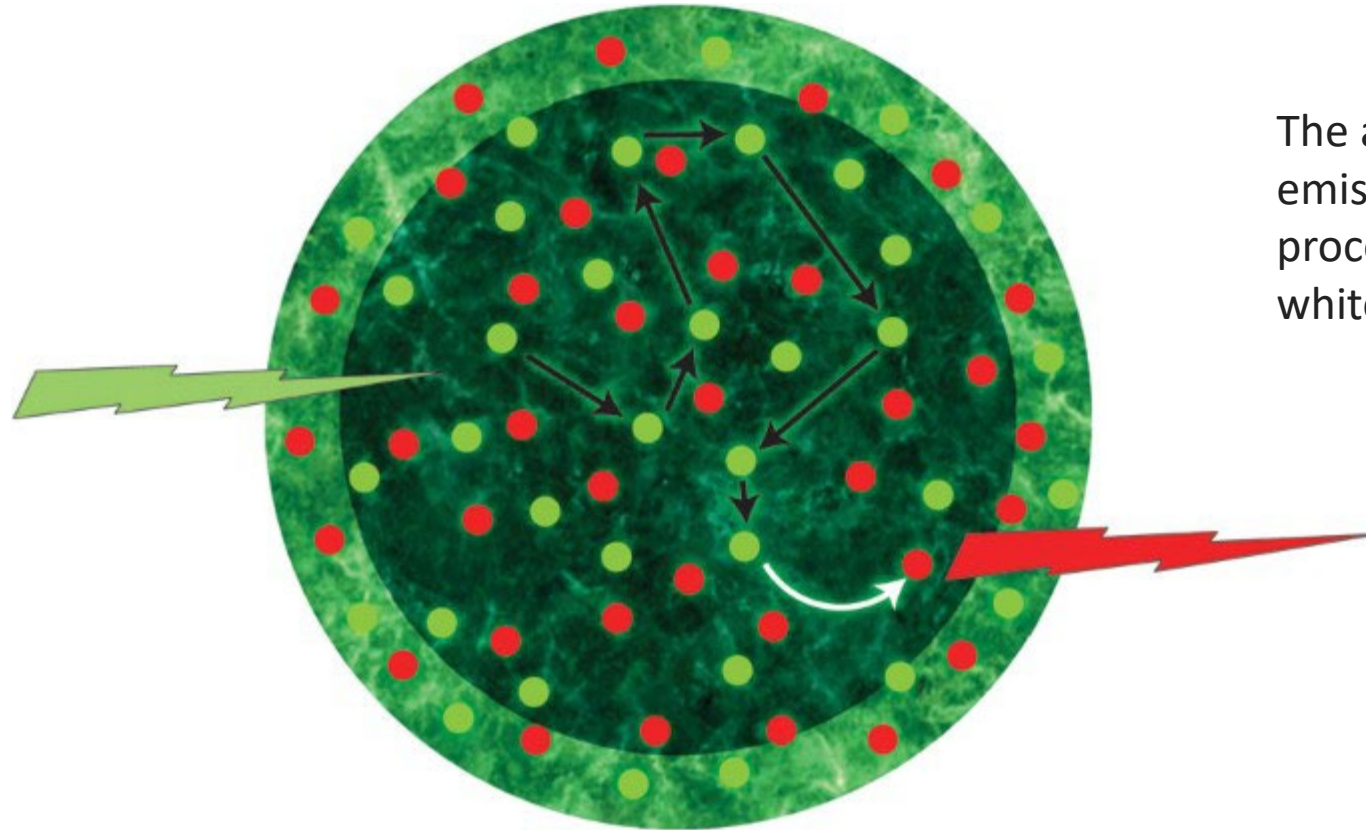
Plastic Solar Cells: Self-Assembly of Bulk Heterojunction Nano-materials by Spontaneous Phase Separation

**Alan HEEGER**  
**Nobel Prize in chemistry 2000**

Professor of Physics, Professor of Materials  
University of California, Santa Barbara

Thursday, October 15<sup>th</sup>, 2015, 18:30, Grand Auditorium, School of Physics

## Dye lasers with energy transfer



The arrows indicate the pumping (green), emission (red) and internal FRET energy-transfer processes (homo-FRET in black and hetero-FRET in white).

# Some future challenges

## *Energy transfer*

### **Distinguishing energy vs. electron transfer**

- Spectroscopic signatures of EnT can overlap with **electron transfer, exciplex formation or charge-transfer states**.
- Unambiguous assignment of mechanisms (Förster, Dexter, coherent transfer) is often difficult.

### **Distinguish between Förster and Dexter EnT in the “intermediate” region (mixed transfer)**

### **EnT in systems with static and/or dynamic disorder (e.g. orientation and distance dependence, aggregation)**

### **Effect of the environment in EnT**

### **Ultrafast and coherent energy transfer and correlation to steady-state measurements**

### **Competing pathways and losses (effect of traps, exciton-exciton annihilation at high-exciton dens.)**

### **Design and control**

- Rational design of systems with **predictable energy transfer pathways**.
- Tuning spectral overlap, coupling strength, and excited-state lifetimes simultaneously.

## *Electron transfer*

### **Theory and experiment**

- Marcus theory in the case of strong coupling
- Ultrafast (sub-ps) ET
- Through-space vs through-bond transfer
- Incorporating nuclear quantum effects, solvent dynamics, and non-equilibrium effects remains difficult.

### **Role of the environment (solvent reorganization, interfaces, proteins, solids, delocalization in crystalline systems)**

### **Ultrafast and non-adiabatic dynamics**

### **Long-range electron transfer (distance dependence of tunneling)**

### **Electron transfer in complex systems**

- ET in biological systems (enzymes, photosynthesis) involves:
- Conformational dynamics
- Multiple competing pathways
- ET in disordered materials suffers from energetic and structural heterogeneity.

### **Distinguishing ET from competing processes (energy transfer, solvation, exciton migration).**

### **Design challenges**

- Rationally designing molecules and materials with tailored ET rates for organic photovoltaics, charge transport layers.